

**ASSESSMENT AND REMEDIATION OF SELECTED HEAVY METAL
CONTAMINANTS IN LEATHER TANNING EFFLUENTS USING GREEN BANANA
PEELS AND COFFEE HUSKS BIOCHAR**

BY

**TENDO IVAN OKUMU
REG. NO 21/U/GMCH/14638/PE**

**A DISSERTATION SUBMITTED TO THE DIRECTORATE OF RESEARCH AND
GRADUATE TRAINING IN PARTIAL FULFILMENT OF THE
REQUIREMENTS FOR THE AWARD OF DEGREE OF
MASTER OF SCIENCE IN CHEMISTRY OF
KYAMBOGO UNIVERSITY**

AUGUST, 2024

DECLARATION

I, **TENDO IVAN OKUMU** hereby declare that this dissertation report titled “***ASSESSMENT AND REMEDIATION OF SELECTED HEAVY METAL CONTAMINANTS IN LEATHER TANNING EFFLUENTS USING GREEN BANANA PEELS AND COFFEE HUSKS BIOCHAR***” is my original work and has never been presented for a degree in any other university.

Name.....

Signature:

Date:

APPROVAL

We as University supervisors confirm that the dissertation titled “***ASSESSMENT AND REMEDIATION OF SELECTED HEAVY METAL CONTAMINANTS IN LEATHER TANNING EFFLUENTS USING GREEN BANANA PEELS AND COFFEE HUSKS BIOCHAR***” has been done by the candidate under our supervision.

Signature:

Date:

Dr. Grace Kizito Bakayita

Principal investigator

Department of Environmental Science

Kyambogo University

Signature:

Date:

Dr. Mary Therese Kaggwa

Co- Principal Investigator

Department of Environmental Science

Kyambogo University

DEDICATION

I dedicate this work to my wife, children and parents who have encouraged and prayed for me continuously throughout my studies.

ACKNOWLEDGEMENTS

I give glory and honor to God Almighty for His providence and protection throughout these studies.

I would also like to extend my heartfelt and sincere gratitude to my research supervisors, Dr. Grace Kizito Bakyayita and Dr. Mary Therese Kaggwa for their tireless effort and guidance throughout this research.

I thank my wife Mrs Okumu Daphine Dusabe for the moral and mental support accorded to me during my study time. Lots of love to my parents Mr and Mrs Okumu for their unconditional love and support. I also heartfully thank my children for their patience during the time I was studying. Thanks to my colleagues for all the discussions and moral support.

I am extremely grateful to the Fuel marking and quality monitoring fraternity for enabling me to successfully carry out my research.

Lastly but not least thanks to Mr. Nyombi Herbert for the advice and guidance that enabled me to finish this research successfully.

TABLE OF CONTENTS

DECLARATION	i
APPROVAL	ii
DEDICATION	iii
ACKNOWLEDGEMENTS	iv
LIST OF FIGURES	viii
LIST OF TABLES	ix
LIST OF APPENDICES	x
OPERATIONAL DEFINITION OF ACRONYMS	xi
ABSTRACT	xii
CHAPTER ONE: INTRODUCTION	1
1.1 Background of the study	1
1.2 Statement of the research problem.....	4
1.3 Objectives of the study.....	4
1.3.1 General objective	4
1.3.2 Specific objectives	4
1.4 Research Hypothesis.....	5
1.5 Justification	5
1.6 Significance of the study.....	6
1.7 Scope of the study	6
CHAPTER TWO: LITERATURE REVIEW	8
2.1 Overview of leather tanning Industry	8
2.2 Environmental concerns in leather tanning.....	9

2.3	Effluent treatment in the leather tanning industries	11
2.4	Characterization of tannery wastewater	12
2.5	Tannery contaminants effects and adsorption.....	14
2.6	Biochar production process.....	16
CHAPTER THREE: MATERIALS AND METHODS		18
3.1	Study Area	18
3.2	Research design	19
3.3	Materials	19
3.4	Methods.....	20
3.4.1	Physico-chemical properties of tannery effluent	20
3.4.2	Laboratory tannery effluent analysis	20
3.4.3	Testing for heavy metal concentrations	23
3.4.4	Preparation of biochar.....	24
3.4.5	Characterization of biochar.....	24
3.4.6	Biosorption experiments	25
3.5	Data analysis	26
CHAPTER FOUR: RESULTS AND DISCUSSIONS.....		27
4.1	Heavy metal concentration in tannery effluent.....	27
4.2	Toxicity of tannery effluent from selected sites	30
4.3	Biochar characterization using Green banana peels and Coffee husks.....	32
4.3.1	Hawk pyrolysis characterization of biochar	32
4.3.2	FTIR characterization of biochar	34

4.4	Effectiveness of selected natural bio-sorbents in removing heavy metal ions from tannery effluents	46
4.4.1	Properties and potential adsorption capacities of bio-sorbent	46
4.4.2	Heavy metal effectiveness removal by the natural bio-absorbent	49
CHAPTER FIVE: CONCLUSIONS AND RECOMMENDATIONS		52
5.1	Conclusion	52
5.2	Recommendations	52
REFERENCES.....		53
APPENDICES		66
Appendix I: Selected heavy metal concentration of water at tannery effluent disposal points.		66
Appendix II: Hawk Analysis Results Of Characterization Of Biochar.		67
Appendix III: Chromium remediation at 20 minutes contact time.		68
Appendix IV: Chromium remediation at 40 minutes contact time		69
Appendix V: Chromium remediation at 60 minutes contact time.		70
Appendix VI: Chromium remediation at 80 minutes contact time.		71

LIST OF FIGURES

Figure 1: Graphical abstract.....	3
Figure 2: The Shimadzu FTIR spectrophotometer was used to identify functional groups.	25
Figure 3: Expected vs observed trends of chromium accumulation in water at tannery effluent discharge point.	29
Figure 4: The Transmission spectrum for the untreated coffee husks biochar.	37
Figure 5: The Transmission spectrum for the treated coffee husks biochar.	38
Figure 6: The transmission spectrum for the untreated banana peels biochar.	41
Figure 7: The transmission spectrum for the treated banana peels biochar.	42
Figure 8: The transmission spectrum for the untreated coffee husks and banana peels biochar. .	44
Figure 9: The Transmission spectrum for the treated coffee husks and banana peels biochar.....	45
Figure 10: Biochar Characterization.	47
Figure 11: Chromium percentage removal vs contact time.	50

LIST OF TABLES

Table 1 : Heavy metals concentrations in the selected tannery sites	27
Table 2: Toxicity of tannery effluent collected at selected sites in Uganda	31
Table 3: Biochar characterization using the hawk pyrolysis machine.....	33
Table 4:Correlation between the proportion removed and the pyrolysis parameter.....	33
Table 5: FTIR characterization of the biochar	35
Table 6: Correlation between stretching bonds and percentage removed	35

LIST OF APPENDICES

Appendix I: Selected heavy metal concentration of water at tannery effluent disposal points	66
Appendix II: Hawk Analysis Results Of Characterization Of Bio char	67
Appendix III: Chromium remediation at 20 minutes contact time	68
Appendix IV: Chromium remediation at 40 minutes contact time.....	69
Appendix V: Chromium remediation at 60 minutes contact time	70
Appendix VI: Chromium remediation at 80 minutes contact time.....	71

OPERATIONAL DEFINITION OF ACRONYMS

AI	Adsorption Index
ANOVA	Analysis of Variance
APHA	American Public Health Association
AQC	Analytical Quality Control
CC	Carbonated Carbon
HI	Hydrogen Index
ICPOES	Inductively Coupled Plasma -Optical Emission Spectrometer
TCH	Treated Coffee Husks Biochar
TBP	Treated Green Banana Peels Biochar
NTCH	Non-Treated Coffee Husks Biochar
NMBP	Non-Treated Green Banana Peels Biochar
OI	Oxygen Index
OSI	Oil Saturation Index
QS	Quality Standard
TOC	Total Organic Carbon

ABSTRACT

Water is undeniably a vital resource for life and a necessity for chemical, physical, biological and economic activities. However, discharge of untreated tannery effluents into water sources has tremendously contributed to water pollution thereby making environmental protection a core demand. This has further led to accumulation of non-degradable heavy metals such as chromium leading to adverse effects on the environment, human health and the economy. The trend of heavy metal concentration increase was expected with tanneries having large production capacities polluting more, results of the study however showed site 3 with the lowest production capacity (50 hides per day) having Cr (chromium) concentration levels of 6.13 ± 0.44 mg/L and Site 1 with a production capacity of 42 tones hides per day, site 2 with a capacity of producing 700 hides and 2500 skins per day containing Cr concentration levels of 0.09 ± 0.18 mg/L and 0.06 ± 0.16 mg/L respectively. Various existing treatment methods employed are either very expensive, time consuming or inadequate hence this study on the remediation of selected heavy metal contaminants in tannery effluents using biochar from green banana peels and coffee husks biomass wastes. Characterization of biochar using hawk pyrolysis machine to determine Total organic carbon (TOC), carbonated carbon (CC), Hydrogen Index (HI), Oxygen Index (OI), Oil Saturation Index (OSI) parameters and FTIR (Fourier transform infrared spectroscopy) studies for functional groups were performed with the aid of a Shimadzu FTIR spectrophotometer. Comparative studies of treated and untreated biochar showed that using non-treated coffee husks biochar is more effective than other studied biochar. Study results further showed that non-treated coffee husks biochar containing TOC-36.76 (wt.%), HI-260, OI-156, CC-1.69 (wt.%), OSI-94.00 per gram sample and Surface O-H stretching (3362 cm^{-1}), Aliphatic C-H stretching (2930.94 cm^{-1}), Aldehyde C-H stretching (2860.23 cm^{-1}), Aliphatic acid C=O stretching (1734.3 cm^{-1}), Unsaturated group like alkene stretching (1655.14 cm^{-1}), Carboxylate anion C=O stretching (1364.62 cm^{-1}), Si-O stretching (1030 cm^{-1}), and Aromatic C-NO₂ stretching (1469.92 cm^{-1}) was the most effective in extracting chromium heavy metal ions from tannery wastewater at a contact time of 60 minutes, remediating 98.3% of chromium. Therefore, tannery industries in Uganda should reconsider taking up this effective alternative as a means of effluent treatment.

Key words; Water pollution, Biochar, Tannery effluents, chromium.

CHAPTER ONE: INTRODUCTION

1.1 Background of the study

Tanneries play a significant role in the economy, contributing to job creation and industrial growth. The global leather trade generates around 150 billion dollars annually, highlighting the economic importance of the industry (Morera et al., 2023). Tanneries also provide employment opportunities in both developed and developing countries, contributing to the economic flow (Caroline et al., 2022). In East Africa, the leather industry hosts 3% of the world's total hides equivalent to 74.7 million cattle with Tanzania holding the lead having 30.5 million cattle, followed by Kenya with 17.5 million cattle, next comes Uganda with a total of 12.8 million cattle and Sudan, Rwanda, Burundi having 11.7 million cattle, 1.3 million cattle 0.801 million cattle respectively. Only 10% of this resource is exported in processed form and of which 90% in raw or semi processed form (East African Leather report, 2009). In Uganda approximately 95% of hides and skins are exported as partially processed leather (wet blue), (Magona, 2022). Between 2008 to 2012 it is estimated, Uganda produced on average 1.6 million hides and 4.7 million skins per year equivalent to 25,600 metric tonnes and 9,400 metric tonnes respectively (Uganda National leather Policy 2015). Currently, Uganda has a limited number of operational tanneries, with the majority of the leather sector's exports in raw or semi-processed form, leading to a significant loss in export revenue (Temsch & Marchich, 2002). The tanning industry in Uganda also grapples with environmental challenges, as tannery effluents which refers to wastewater that has undergone some form of treatment and is ready for discharge or further processing, need to comply with local and international environmental standards for sustainable production. The tanning process can be divided into three major parts which include pre tanning, tanning and post tanning. This can be split further into six main stages with each contributing to contamination and pollution. (Dessinioti & Stratigos, 2022).

Preparation of the hides and skins from the slaughter houses. Here the hides are treated with salts, insecticides and bactericides which contain heavy metals such as lead, nickel, mercury, copper, arsenic and zinc as formulations or contaminants. (Sawalha et al., 2020; Dharmaraj et al., 2021). Effluents from this stage contains wastewater, BOD (Biological oxygen demand), COD (Chemical oxygen demand), salts and heavy metals as effluents. (Arti & Mehra, 2023)

Further treatments involve soaking, liming, deliming and bating using alkali, surfactants, ammonium sulphate, acids and enzymes producing an effluent containing wastewater, BOD, COD, Ammonia, Organic Nitrates, Suspended solids and sulphides (Patel et al., 2021). Pickling and Chrome tanning employs chromium (III), sodium chloride, Acids, fungicides and releases BOD, COD, Chromium, Fungicides (Sawalha et al., 2020). Such elements stem from a wide range of chemicals used by the tanning industry that are harmful to biota and humans (Tadesse, 2017). According to Asaduzzaman et al., (2014), the chromium (III) salts are added to fixate the Cr tanning based on the cross-linkage of Cr ions with free carboxyl groups in the collagen making the hide resistant to bacteria and high temperatures. The finishing stage uses Dyes, fats and liquors to give a durable leather product and this stage disposes chromium, COD, BOD, solid finisher residues and TDS(Total dissolved solids) in wastewater. On the other hand, biosorbent from agricultural wastes; green banana peels (*Musa spp*), and coffee husks (*Coffea canephora*) can provide a low-cost alternative material for the uptake of aqueous heavy metal ions in minute concentrations to achieve the allowable concentration limits in treated wastewater.

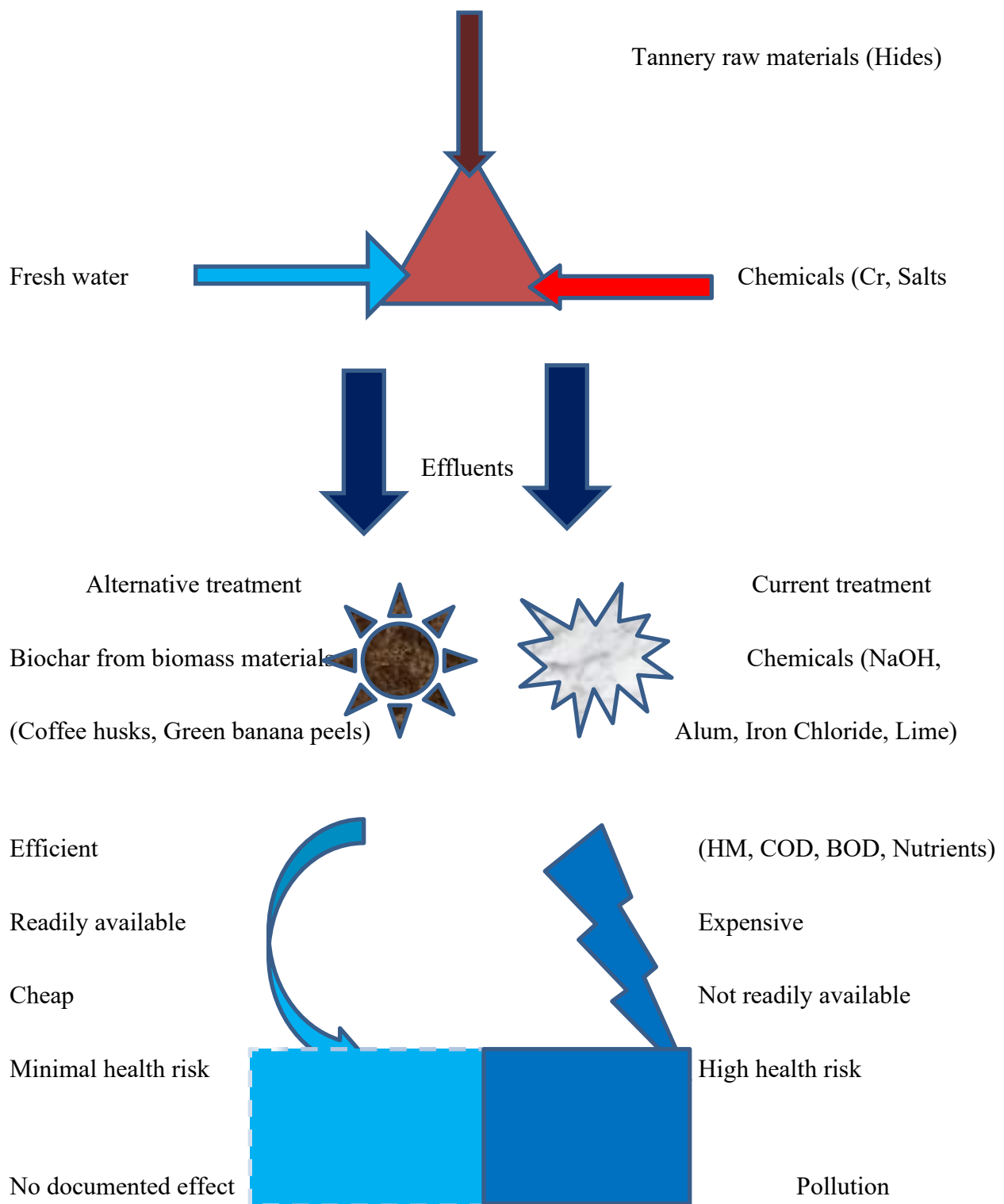


Figure 1: Graphical abstract

1.2 Statement of the research problem

Earlier studies by various scholars (Bishnoi, Kumar and Rami, 2007; Haroun, Idris & Omer, 2007; Mwinyihinja, 2010) have indicated that tannery wastewater is contaminated with chrome and trace metals at levels above the allowable limits, which impacts the environment and human health. The hides and skin tanning industry has grown in capacity and output and its chrome consumption has increased but the rate of chrome recovery, reuse and recycling are low.

The leather tanning industry therefore releases partially treated contaminated tannery effluents that negatively impact the quality of water in the receiving streams, rivers, and lakes as well as expose the aquatic and terrestrial ecosystems that depend on those water resources to health risks. The population also depends on streams, rivers, and lakes for the provision of water for domestic and industrial purposes and fish resources for food.

The environment and health risks usually manifest after chronic exposure to minute quantities of chrome and other heavy metal contaminants in various trophic levels in the ecosystem and when the bioaccumulation of the contaminants occurs. Therefore, the need to develop local environmentally acceptable and sustainable biosorbent filters for the remediation of chrome and trace metals in tannery effluents to acceptable water quality standards.

1.3 Objectives of the study

1.3.1 General objective

The general objective was to evaluate the levels of selected contaminants (Cr, Ni, Zn, Cu, Pb, pH, EC, TDS, SO_4^{2-} , Cl^- , reactive PO_4^{3-} , NO_3^- , NH_4^+ , TN, P, BOD, COD, TSS and turbidity) in tannery effluents and to remediate the heavy metals using biochar.

1.3.2 Specific objectives

The specific objectives were to;

- 1) Determine the levels of selected heavy metals and nutrients in tannery wastewater from Sky fat Company Limited in Jinja, Leather Industries of Uganda in Jinja and Kobs brands (U) Limited in Bukasa Kirinya, Wakiso.
- 2) Characterize biochar of green banana peels and coffee husks.
- 3) Study the effectiveness of green banana peels and coffee husks biochar when used as natural bio-sorbents in removing heavy metal ions from discharged tannery effluents in batch studies.

1.4 Research Hypothesis

The research hypotheses that guided the study were;

1. Ho: There is no significant difference in the levels and toxicity of selected heavy metals and nutrients in tannery wastewater from chosen tannery industries.
2. Ho: There is no significant difference in characteristics of the biochar produced from green banana peels and that from coffee husks.
3. Ho: There is no significant difference in the effectiveness of green banana peels and coffee husks biochar when used as natural bio-sorbents in removing heavy metal ions from discharged tannery effluents in batch studies.

1.5 Justification

Over 80 countries in the world suffer from a water deficit, and an estimated 1.2 billion people drink unclean water. Water scarcity is an evolving challenge that is caused by polluting the limited resources. Tannery industry is one of the main polluters and consumers of the valuable water resource. The industry releases huge amounts of highly polluted water into the environment. The cost of water treatment is increasing and the quality of river water is not stable due to suspended and colloidal particle load. Developing countries pay a high cost to import chemicals for water treatment. However, the use of biomass wastes to remediate tannery effluents is a good alternative measure since it's in line with Sustainable development goal 12 (SDG 12) which promotes the principle of circular economy through waste management . It can also effectively remove metal ions from solutions with low concentrations thus addressing (SDG 6) that promotes proper wastewater treatment, improving the quality of water for drinking. SDG 3(Good health and

wellbeing) is also achieved when the population accesses clean and safe water preventing water related diseases. This study therefore, investigated the potential of *Musa spp* peels (Green banana peels) and *Coffea canephora* husks (Coffee husks) biochar in removing heavy metal in tannery effluents.

1.6 Significance of the study

The study determined concentration levels, and toxicity of selected heavy metals and nutrients in tannery wastewater which was crucial for understanding the extent of contamination and its potential effects on the environment and public health. This information is essential for developing targeted remediation strategies and regulatory measures to mitigate the adverse impacts of heavy metal pollution. In addition, the study further, prepares and characterizes biochar using green banana peels and coffee husks thus offering a sustainable solution for waste management. By converting these agricultural by-products into biochar, the study contributes to waste reduction and the generation of value-added products, aligning with the principles of circular economy and sustainable development. Further, the study determined the effectiveness of green banana peels and coffee husks biochar as filter media in batch studies for remediating selected heavy metal ions from contaminated tannery industrial wastewater addressing the need for cost-effective and eco-friendly remediation techniques. If proven effective, bio char could serve as a viable alternative to conventional treatment methods, offering a sustainable and affordable means of purifying tannery wastewater. The results of the study will contribute to the development of sustainable and effective strategies for assessing and remediating heavy metal contaminants in tannery wastewater, while also addressing waste management and resource utilization challenges. The findings of this research could have far-reaching implications for environmental protection, public health, and sustainable industrial practices in Uganda and beyond.

1.7 Scope of the study

The study was undertaken in Jinja and Wakiso districts of Uganda where tannery effluents was collected from three specific sites, namely site 1, 2 and 3. These sites were chosen to represent a diverse range of tannery operations and wastewater compositions, providing a comprehensive understanding of heavy metal contamination in tannery wastewaters within the region.

This study took place from January 2023 to December 2024, allowing for a comprehensive assessment and remediation of heavy metal contaminants in tannery wastewaters over the course of two years. This duration provided ample time for data collection, analysis, and the implementation of remediation strategies.

The study primarily focused on the assessment and remediation of heavy metal contaminants in tannery wastewaters. This included the evaluation of concentration levels, and toxicity of selected heavy metals, as well as the preparation and characterization of biochar using green banana peels and coffee husks. Additionally, the study involved the determination of the effectiveness of biochar as a filter media in batch studies for remediating selected heavy metal ions from contaminated tannery industrial wastewater. The assessment of the synergistic effects and implications of combining biochar derived from two different waste biomasses on the extraction of heavy metals from tannery wastewater was also within the study's scope.

CHAPTER TWO: LITERATURE REVIEW

2.1 Overview of leather tanning Industry

According to NAPE, (2009), leather tanning is a process of converting decomposable skin into leather that is usually non decomposable in a short term. This is usually done with tannin - an acidic chemical compound that prevents decomposition. Leather tanning is important for converting hides and skins into usable materials for production of leather-based consumer products. The leather tanning industry has an ancient history dating back to the beginning of time. According to biblical accounts Genesis 3:21 Good news bible, “And the Lord God made clothes out of animal skins for Adam and his wife, and he clothed them”. The ancient Egyptians, Greeks and Romans all used leather extensively for various purposes including military protection gear.

During the middle Ages the leather industry grew in Europe especially in Spain and Italy. Tanneries were established and techniques for leather refining were established. Industrial revolution brought significant changes including the use of machinery which improved on leather production efficiency and more harm to the environment. The development of the steam engine led to formation of large-scale production tanneries. The leather industry continued to evolve throughout the 20th century with advances in technology till today when it is a major global industry valued at \$ 414 billion in 2020 and is expected to reach \$ 754 billion by 2028 growing at a rate of 7.4% from 2021 to 2025.

Uganda currently has four bovine tanneries and one fish skin tannery are owned by foreign investors (NAPE, 2009) and a government backed leather processing factory at Kawumu in Luweero district. The tanneries include; Sky Fat Tannery Co. Ltd (SFT), Balawi Hides and Skins, Leather Industries of Uganda (LIU), and Novelty Investment Tannery Ltd. There is one tannery in Jinja district that processes fish skins into leather, under the names of Uganda Fish Leather Tannery Ltd. Uganda Leather Industries Ltd in Jinja Produces Wet blue and finished leather. Sky Fat Tannery Co. Ltd (SFT) located in Jinja also produces Wet Blue Hides and Wet Blue Skins. Novelty Investment Tannery Ltd in Masaka district produces Wet blue Hides and skins. Uganda Fish Leather Tannery Ltd situated in Jinja, Crust and finished skin from Nile Perch. Balawi Hides and Skins produces Wet blue and Hides/skins in Busia District. Kawumu Leather industry launched in 2022 in Luweero district produces finished leather products. Kobs Industries located at Bukasa

Kirinya produces leather shoes at a very small scale. SWT Tanners Ltd. (Under construction) - Jinja District. The installed capacity of these tanneries is estimated at about 1.1 million hides and 2.1 million skins per annum. Government is promoting production and export of finished leather and leather products to maximise revenue from the leather business. A levy on export of raw hides and skins has been introduced to help government reduce export of raw hides and skins and promote the production of finished leather and leather products. (Hides and skins export duty Amendment Act, 2025).

The livestock industry amidst continuous challenges greatly contributes to the leather industry in Uganda. In 2008, the National Environment Management Authority (NEMA) ordered the closure of two tanneries in Jinja town over poor disposal of effluents that were leading to pollution of the environment. In March 2008, the National Water and Sewerage Corporation (NWSC) closed off all sewage lines from two leather-tannery industries, which had persistently refused to comply with set effluent standards. (Leather International, 2008). Earlier on, government had closed the leather tannery in Mbarara district for failure to meet the required environmental standards. Continued growth of the industry in the country under a liberalized economy has also dictated the need for effective and well-equipped regulating institutions.

The annual production of hides and skins had grown to an estimated 1.2 million hides and 2 million skins over the years, (NAPE 2009). The leather industry is increasingly being recognized as an area of great economic potential. Uganda's leather is characterized as being of high quality and of heavy substance. Uganda bovine hides have a distinct advantage because of their high texture and heavy substance that make them suitable for production of heavy upper leather and vegetable tanned sole leather. Over 90 per cent of the exported hides and skins from Uganda are usually in their raw form; mainly air-dried and some wet-salted. The bovine hides (fresh, dried or salted) and leather forms the bulk of the hides, skins and leather export trade.

2.2 Environmental concerns in leather tanning

NAPE (2009) reported that industrial effluents from the tannery industry are a major environmental and health concern in many African countries. They argued that tannery wastewaters contain large quantities of organic and inorganic compounds; including toxic

substances such as chromium salts. They observed that tannery effluents deteriorate the physical, chemical and biological properties of the receiving surface water. Poorly treated effluents from the tannery industry that is used for irrigation purposes lead to wide spread contamination of food chains, sharp decline in productivity of food crops, soil, vegetables, livestock and even milk production. Heavy metals contamination of surface and ground drinking water has grave public health implications. Chromium, lead, zinc and copper are examples of metals that have been found in sediments affected by tannery effluents.

The primary raw material for leather tanning is derived from slaughter houses and meat industry. Converting the raw material to finished product involves the usage of many chemicals thus making the leather industry an enormous contributor to pollution of the environment with toxic and hazardous chemicals. For instance, in leather tanning one metric ton of raw materials converted into only 200 kg of usable product comprising of 3 kgs of chromium and 50,000 kgs of wastewater containing approximately 5 kgs of mostly chromium and other heavy metals.(Bianca et al., 2015)

Pre-tanning and tanning operations contribute about 90% of the total pollution caused by the leather industries. The pre tanning activities causes fluctuations in pH, thereby increasing the COD, TDS, Chlorides and Sulphides in wastewater discharge by tanneries. During chrome tanning, the poor chromium uptake causes material wastage and results in ecological imbalances. The post tanning process also leads to significant modifications of COD, TDS, and heavy metal Pollution (Thanikaivelan et al., 2015).

One of the most significant environment concerns in leather tanning is the use of hazardous chemicals in the tanning process. Leather is typically tanned using chemicals such as chromium, which can be toxic to humans and the environment. These chemicals can contaminate the air, soil and water leading to environmental degradation and health challenges.

Further, leather tanning requires large amounts of water and the wastewater generated during the process can be highly contaminated with heavy metals and other pollutants. This wastewater can pollute local waterways and harm aquatic ecosystems. Water consumption is between 25-60 m³ per ton of fresh leather and the yield is 500 kilograms of finished leather. Depending on the process

which is unique to each industry, more than 440 kgs of chemicals can be used per ton of leather as described by (Lara et al., 2020)

2.3 Effluent treatment in the leather tanning industries

Studies show that different industries employ different methods to remediate wastewater discharged from various sectors such as textiles, tannery and other wastewater generating businesses. Chowdhury reported three key wastewater treatment methods that included biological, chemical and physical as being mostly employed in the tannery industry. Among the above, the physical treatment methods such as filtration and sedimentation which separate contaminants from wastewater without any chemical change or reaction are widely employed (Savanna et al., 2021). On the other hand, using biological wastewater treatment primarily involves use of microbes such as bacteria and protozoa that clean the water. In this case the, microbes' breakdown large organic waste found in water and convert it to simple compounds via aerobic and anaerobic digestion (Demirbas et al., 2017). However, they further observed that biological methods increase BOD and COD in the effluent discharged. The chemical treatment methods employ chemical reactants to breakdown contaminants in wastewater (Amito et al., 2021). Adsorption has also been used to reduce the content of heavy metals in several treatment procedures using agro based industrial by products as raw materials (Lang et al., 2020). The phenomenon of adsorption has also shown several applications in wastewater treatment such as the removal of heavy metals from solutions and the removal of coloring matter and nutrients from industrial effluents.

Currently, biochar has also been widely applied in wastewater pollution control due to its high stability, excellent surface properties, high-developed pore structure, and rich surface functional groups. Biochar is a carbon rich (65-90%) solid product of biomass pyrolysis that possess a porous structure of char particles enhancing the water retaining capacities and nutrients retention of soil as well as microbial accumulation (Qambrani et al., 2017). The application of bio char is dependent on its physical chemical properties (Jindo et al., 2014). These properties are dependent on the feedstock type and the conditions of the pyrolysis (Sun et al, 2014). Biochar can be used as an adsorbent in separating some chemical species from aqueous solutions (Carrier et al., 2012). Agricultural biomass is considered as the most abundant renewable resource. Main sources and

feedstock of biochar include crop straw and residues, animal manures, fruit pits, twigs, and leaf litter forestry wastes as well as food leftover and bagasse (Shaaban et al., 2018).

2.4 Characterization of tannery wastewater

The quality of water is determined by comparison of the physico-chemical parameters with the legally accepted water quality standards. The untreated wastewater generated from leather tanning can vary greatly depending on the chemicals and treatment processes involved. The tannery effluent always contain a great amount of color, pollutants like materials with a high biological oxygen demand (BOD) and chemical oxygen demand (COD), high total suspended solids (TSS), Total dissolved solids (TDS), nitrogen, chlorides, phosphates, chromium, copper, and/or the salts of other heavy metals; of these, the most important are considered to be chromium, cadmium, lead, zinc, copper, nickel, chemical oxygen demand COD, biological oxygen demand (BOD), pH, nitrogen and phosphorous (Tufekci *et al.*, 2007).

Biological oxygen demand (BOD) is simply defined as the amount of oxygen required by bacteria while stabilizing decomposable organic matter under aerobic conditions. Biochemical oxygen demand has also been defined as a measure of the concentration of organic matter present in any water (Varsha *et al.*, 2013). The determination of BOD is used to measure the purification capacity of streams and serves regulatory authorities as a means of checking the quality of effluents discharged (Patel & Vashi , 2015). Discharge of tannery wastewater into natural water bodies would decrease the oxygen content because of the lower penetration of sunlight and, at the same time, because of the increased biological oxygen demand (BOD) that would lead to an increase in oxygen consumption. Chemical oxygen demand (COD) is defined as the amount of oxygen used while oxidizing the organic matter content of a sample with a strong chemical oxidant under acidic conditions. COD indicates toxic conditions and the presence of biologically resistant organic substances (Patel & Vashi , 2015). Total suspended solids (TSS) levels that define solids in water that can be trapped by a filter are high in raw tannery processing wastewater compared to many other industries (Tufekci, *et al.*, 2007). Total dissolved solids (TDS) are measure of all the compounds dissolved in water and are directly proportional to electrical conductivity (EC). TDS represents the total quantity of organic and inorganic dissolved material in the water (Dallas and Day, 2004).

The basic principle of electronic pH measurement is to determine of hydrogen ions activity by potentiometer measurement using a standard sensing electrode (glass electrode) and a reference electrode (calomel electrode). pH is a measurement of acid-base equilibrium achieved by various dissolved compounds. The pH range of 6-9 reflects biological life. An indication of extreme pH is known to damage biological processes in biological treatment units (Gray, 2002; FAO, 2007). Extreme pH levels reflect presence of particulate matter, accumulation of toxic chemicals, and increasing alkalinity levels that are common problems in wastewater.

Electrical conductivity (EC) is a function of total dissolved solids (TDS) known as ions concentration, which determines the quality of water. Conductivity itself is not a human or aquatic health concern, but because it is easily measured, it can serve as an indicator of other water quality problems. If the conductivity of a stream suddenly increases, it indicates that there is a source of dissolved ions in the vicinity (Tariq *et al.*, 2006). Color is quantified in terms of arbitrary units. Colored waters are objectionable for a number of reasons, not least of which include aesthetic considerations. Furthermore, the presence of coloring matter is an indication of pollution of some form and, therefore, steps are invariably taken to remove color from waters during treatment. However, as far as humic coloring matter is concerned, there is no evidence of a health hazard (Patel & Vashi, 2015)

Heavy metals that define metals with relatively high densities, atomic weight or atomic numbers are poisonous to living organisms including humans due to their bio-toxic effects, which could be acute, chronic or sub chronic, neurotoxic, carcinogenic, mutagenic, or teratogenic (Patel & Vashi, 2015). Heavy metal ions are often present in industrial wastewater and can pose an environmental hazard when discharged uncontrolled. Heavy metals in tanning industry wastewater present a major environmental problem. It has become a common practice to discharge wastewater originating from various production processes of leather industrial units directly into water channels. This indiscriminate discharge of industrial effluents is posing serious threats to human and animal health.

Some possible sources of heavy metals in tannery operations are processing of raw leather, water, chrome tanning, dyestuffs (heavy metals are constituents of some classes of dyes and pigments), finishing chemical impurities, and the plumbing fittings used in dyeing and finishing plant. Heavy

metals are often used as oxidizing agents, as metal complex dyes, dye stripping agents, fastness improvers and finishers (Zeiner, Rezig & Steffan, 2007). Heavy metals may also be found in plant fibers because of absorption from the soil in which they are grow.

The heavy metals concerned are cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), lead (Pb), nickel (Ni), and zinc (Zn), many of which can be found in effluents from tannery operations. Various heavy metals such as Zinc, lead, copper etc., have been reported to pollute the water, thereby making it unfit for human consumption (Nand *et al.*, 2014). High levels of cadmium and Lead found in most tannery effluents. Cadmium is toxic at extremely low levels; it is also associated with bone defects like osteomalacia, increased blood pressure, and myocardial dysfunctions. Severe exposure to cadmium may result in pulmonary edema and death (Patel & Vashi , 2015).

Hexavalent chromium can cause major health problems such as liver and kidney illness, diahrrhea, nose bleeding, dermatitis, mouth ulcers, cancer and a decrease in the number of white blood , reducing the immune system ability to resist diseases. According to several studies done in 2015, over 16 million people were harmed due to Cr(VI) heavy metal pollution. The methods for determining the concentrations of these metals vary in complexity according to the interfering substances that may be present. Typical methods of determining their concentrations include flame atomic absorption, electro thermal atomic absorption, inductively coupled plasma optical emission spectrometry (ICPOES), and inductively coupled plasma (ICP)/ mass spectrometry (APHA, 2001).

2.5 Tannery contaminants effects and adsorption

Akpor & Muchie, (2011) reported eutrophication, increased water purification cost, interference with recreational value of water, health risks to humans and livestock, excessive loss of oxygen and undesirable changes in aquatic populations as the major effects of tannery contaminants. The release of nutrients in a natural water body increases the oxygen consumption and thus decrease the oxygen availability and the life in the water basin (Sharma *et al.*, 2007). In addition, the colored effluent affects the photosynthetic capacity of the ecosystem by reducing the penetration of sunlight into aquatic environments. This affects the growth of plants and other organisms living in

the same ecosystem. The dyes and their degradation products may have genotoxic and mutagenic effect and thus interfere with the genetic material and the reproductive system of vertebrates and invertebrates (Pinheiro *et al.*, 2004; Sharma *et al.*, 2007). Some heavy metals and their transformation products are mutagenic; they can increase the rate of DNA or RNA mutations and thus change their composition. Some mutations can cause cancer, and therefore some mutagenic compounds are also carcinogenic (Punzi, 2015). Untreated or inadequately treated wastewater effluent may lead to eutrophication in receiving water bodies and also create environmental conditions that favor proliferation of waterborne pathogens of toxin-producing cyanobacteria (Akpor & Muchie 2011).

Water resources are continuously decreasing around the world due to various environmental degradation activities, climate change (Konapala *et al.*, 2020). It is necessary to treat wastewater before human consumption especially in regions with high water stress (Aaro, 2020). Various processes and technologies are being researched to improve the quality of water so as to sustain the water requirement. Currently many techniques are used for wastewater treatment including ion exchange, flocculation, coagulation, adsorption, membrane filtration, reverse osmosis. Adsorption has many advantages in comparison to other methods such as high efficiency and effectiveness in removing heavy metals, inexpensive and easy application. Never the less its application has not been wide due to the high production cost of commercial adsorbent such as activated carbon and silica gel hence resulting to the need of readily available and cheap alternatives (Mohamed *et al.*, 2020). Adsorption is the adhesion of molecules, compounds or ions from a gas, liquid or dissolved solid to a surface. This process creates a film of the adsorbate (solute) on the surface of the adsorbent (Solvent). This process differs from absorption in which a fluid (the absorbate) is dissolved by or permeates a liquid or solid (Thesaurus. 2018). Adsorption is a surface phenomenon and does not penetrate through the surface to the bulk of the adsorbent.

One of the most consumed foods in Uganda is the banana, locally known as matooke. It is estimated that an average Ugandan consumes a staggering 350 Kgs per year, almost 1 kg per day. Over the centuries, bananas have evolved into a symbol of cultural identity in some parts of Uganda with over 80 different species grown there. Bananas derived from *Musa acuminata* are majorly used for dessert and are eaten raw while those derived from *Musa balbisiana* are plantains best devoured cooked after peeling off the green starchy cover as a biomass waste which is mostly

discarded off recklessly to the environment. Green banana peels produce materials containing a high content of micro pores, meso pores and macro pores. This highly porous structure can adsorb compounds to its surface and the high surface area is also used for the adsorption of molecules with heavy densities (Achmad et al, 2018)

Another natural absorbent is Coffee. Coffee is the second largest valued commodity in international trade and most widely traded tropical agricultural commodity after petroleum according to the Uganda coffee sector report (2020). In east Africa Uganda carries the mantle of a leading exporter of coffee which amounted to 5,409,054 bags worth \$ 513.99 m. The ripe coffee cherries undergo various process to extract the bean from the pulp covering and basically there two main techniques used i.e. wet processing which the fruit is removed in three stages and dry processing which involves drying the fruits usually under the sun and removal of the dried covering or husks in a mechanical operation. These husks are mostly discarded as wastes or at times utilized for mulching and biomass fuels. Coffee husks contain ligno-cellulosic materials hence can be used as good adsorbents. They also possess a high concentration of minerals such as carbon, silicon and a high volatile content rendering them to generate a rich pore structure and has an effect on the mechanical properties of the formed adsorbent (Achmad et al, 2018)

2.6 Biochar production process

Biochar has been widely applied as an adsorbent to remove heavy metals, nutrients and organic pollutants from waste water. Compared to activated charcoal, biochar generally has larger surface area, stronger desorption capacity and more abundant surface functional groups which makes it a suitable alternative in various wastewater treatments. Biochar is a porous carbonaceous material produced during the thermochemical decomposition of biomass feedstock in the presence of little or no oxygen. Biomass feedstock can be any organic waste material which include agricultural residues, sewage solid wastes or municipal solid waste (Colantoni et al., 2016; Xiong et al., 2019).

Methods for thermochemical decomposition include pyrolysis, microwave heating, gasification, torrefaction and hydrothermal carbonization, varying in thermal chemical temperature and duration (Mohan et al., 2014; Fang et al., 2018). The use of biochar in wastewater treatment is mostly based on two distinct benefits: 1. Biochar production can offset greenhouse gas emission

because it stores carbon in a stable form, preventing the release of greenhouse gases into the atmosphere from biomass degradation (Creamer and Gao, 2016; Yang et al., 2018a). 2. Biochar is an effective, low cost and environment friendly adsorbent (Cha et al., 2016; Inyang et al., 2016), which is related to its relatively large surface area and abundant surface functional groups (Wang et al., 2017).

Previous studies have shown biochar properties are affected by feedstock type, pretreatment and post treatments (Wang et al., 2017). Pretreatments vary depending on feedstock and the purposes of bio char use, including physical (dry, crush, sieve, wash etc.), chemical (treat with chemicals or functional materials, load of precursors and functional agents, etc.), and biological (bacterial treatment, etc.). Post treatments mainly rely on physical (ball milling, magnetization, etc.) and chemical (corrosive treatment, etc.) methods (Zhang and GAO, 2013; Usman et al., 2016). Also, the thermochemical decomposition methods and their temperature and duration can significantly affect biochar physical and chemical properties (Yu et al., 2019).

Biochar has a high adsorption efficiency and removes heavy metals, organics and inorganics from wastewater (Liang et al., 2021; Tan et al., 2015). Biochar preparation can offset greenhouse gas emission because it stores carbon in a stable form, preventing the release of greenhouse gases into the atmosphere from biomass degradation (Creamer and Gao, 2016; Yang et al., 2018). Biochar is readily available, cheap to access and prepare and environmentally friendly on the other hand the use of other artificial elements is expensive and hazardous to the environment.

CHAPTER THREE: MATERIALS AND METHODS

3.1 Study Area

The study was undertaken in Jinja City, and Wakiso district of Uganda as these are the key areas with major tannery establishments in the country hence their inhabitants ought to face direct impact from tannery effluent discharge into the surrounding water sources. The effluent studied was collected from three tannery sites selected based on their accessibility and direct impact on the growing urban population of Uganda as they discharge in key domestic support water bodies used by the majority of citizens in the country. These included Sky Fat company Limited (Site 1), and Leather industries of Uganda (Site 2) in Jinja City and Kob brands Uganda limited (Site 3) in Wakiso district.

Site 1 is a Chinese owned leather tannery industry that is located in the Eastern town of Jinja. The tannery was initially connected to the National Water and Sewerage Corporation sewer system but it has recently put in place its own waste treatment plant to conform to environmental regulations. The industry was initially allowed to dispose its industrial effluents in the municipal landfill but it was able to acquire land for disposal of its solid wastes in 2008 where it is currently constructing its own landfill. Site 1 finds it difficult to get all the chemicals that it requires to treat the waste because chemicals in Uganda are more expensive than in many parts of the world. The industry mainly supplies its leather to the Chinese market and not any other market because their quality of products can only meet the Chinese standards. Site 1 is the leading exporter of wet blue and unprocessed hides and skins in the country) although this was greatly affected by the global economic crisis.

Site 2 is also located in Jinja and is owned by the Industrial Promotion Services (IPS) of the Agha Khan group of companies and it is probably one of the oldest leather tanning industries in Uganda. The Agha Khan operates leather-tanneries in the three East African countries of Kenya, Uganda and Tanzania. The industry has a processing capacity of 300 tonnes of hides per month and a capacity for 700 hides and 2500 skins per day. It is the only leather tannery industry in Uganda that has capacity to process hides and skins into leather. Site 2 can produce about 100,000 square ft per month of finished leather mainly for export and about 1000 hides per month of finished

leather for the domestic market. LIU is probably one of the leather tannery industries that use a lot of chemicals

Site 3 is located in Bukasa Kirinya, Wakiso. It started in 2016 and specialises in manufacturing of leather shoes. For every 20 pairs of men shoes or 40 pairs of women shoes, one hide is utilised. Unfortunately, Site 3 have no effluent treatment plant and discharges its effluents into Bukasa wetland.

3.2 Research design

The study undertook a quantitative research design. In particular, it took an experimental research approach. The use of quantitative methodology availed results that were replicated and therefore generalized for a larger population for future studies with certainty. More research indicates that the quantitative methodology is more important as a scientific methodology because it ensures that the results have a measurable efficiency that can be graded in accordance to their efficacy. The study included experimentation, precise control of variables, cause and effects determined based on the results. The results were duplicated to create real life solutions based on the findings.

3.3 Materials

Preparation of the different materials needed for the study was done based on their characteristics and time required for each. Treated Jars were used to collect tannery effluent from the different industries selected for the study. The jars were labelled according to their source, date and time of collection and transported in cool boxes for experimentation, testing and analysis in the laboratory. The collected tannery effluent samples were subjected to different chemicals in the laboratory ascertain the levels of different heavy metal after various treatments. The standard solutions and reagents used for effluent sample testing were laboratory prepared in accordance to standard operating procedures. The biomass materials used were green banana peels and coffee husks, which were collected from Kalerwe market and Kawempe coffee processing factory in Uganda.

3.4 Methods

3.4.1 Physico-chemical properties of tannery effluent

Tannery effluent samples were collected from three purposively selected sites. Three effluent samples were collected from each site both in the dry (June-August 2022) and wet season (March-May 2022). Each effluent sample was collected in the afternoon (12:00 noon) during each time of sample collection. Water physico-chemical properties such as pH, Electrical Conductivity and Turbidity were measured *in-situ* using a portable field water testing tool Kit (Wagtech MAJIMETER, WAG-WE 51000, UK) according to the manufacturer's instruction.

Effluent samples were collected directly from the discharge points using clean plastic beakers of 250 ml that were first rinsed with distilled water in between samples and then put in a 1 litre plastic jerrican with respective site label and delivered to the laboratory for analysis of the physico-chemical parameters (TSS, COD, TP, TN and TDS). All collected water samples were kept in an ice box at 4 °C and transported to National Water Quality Reference Laboratory, Entebbe for analysis within 24 hours. All samples were stored and handled according to Standard Methods for the Examination of Water and Wastewater (APHA, 2017).

3.4.2 Laboratory tannery effluent analysis

Laboratory tannery effluent analysis was performed according to standard methods for the examination of water and wastewater (23rd Edition) (Baird & Bridgewater, 2017). All laboratory glassware was acid cleaned using 20% HCl for nutrient measurements, and HNO₃ (2%) for trace metals measurements. The parameters analyzed were COD, TSS, and TDS as elaborated in the subsequent sections

Chemical Oxygen Demand determination

Chemical oxygen demand was determined using the closed reflux calorimetry method. Here potassium dichromate reagent mixed with sulphuric acid and mercuric sulfate was used to mask chloride which consumes the dichromate ions hence giving high false values. The excess dichromate which remains unreacted after a 2 hours of reaction process was titrated and measured spectrophotometrically.

In this method, 2 mL of each water sample was pipetted and put into a digestion tube. The tubes were capped tightly and gently mixed. They were then placed in a digestion block maintained at 150 °C for 2 hours after which the tubes were removed, swirled to mix and then cooled at room temperature. The results were measured spectrophotometrically on a DR 6000 (Hach USA) at a wavelength of 620 nm.

Determination of Total Suspended Solids

Total suspended solids (TSS) in collected stream water were determined gravimetrically. Here an empty filter paper was washed, dried in an oven, its weight taken and recorded. A well-mixed sample was then filtered through the filter paper. The filter paper containing the residue was dried in an oven for 30 minutes at 105 °C for till constant weight. Thereafter, the filter paper's weight was recorded. The difference in weight between the empty filter paper and the filter paper containing the residue was calculated and recorded as TSS in mg/L.

Determination of Total Dissolved Solids

Concentrations of total dissolved solids (TDS) in collected stream water samples were carried out according to the standard methods for the examination of water and wastewater (APHA, 2017) and Sawyer *et al.*, (1994) following the gravimetric method. A fixed volume of water sample was poured on a pre-weighed glass fiber filter of a specified pore size before starting the vacuum filtration process. The filter was removed after the completion of the filtration process and placed in an aluminum dish in an oven at 100 °C for 2-3 hours to completely dry off the remaining water.

Total Nitrogen

Total nitrogen (TN) was measured following the standard method for examination of water and wastewater (23rd Edition) (Baird & Bridgewater, 2017). 10 mL of a sample was transferred into the digestion vial, and then one micro spoon of ammonium per sulphate and six drops of sodium hydroxide was added and shaken for uniformity. The sample was later digested in an auto clave for two hours at 121 °C. After that the samples were run on the Gallery Plus discrete analyzer which gives the value of TN in mg/L.

Total Phosphorus

Total phosphorus was measured on the Gallery Plus Discrete analyzer. Prior to this, 10 mL of sample was transferred into a digestion vial, then one micro spoon of ammonium per sulphate was added followed by 6 drops of sodium hydroxide and taken to the autoclave for digestion for 2 hours. The samples were run on the Gallery plus analyzer which gives phosphate concentration in mg/L.

Nitrates and ammonia

The Nitrates were analyzed using a UV-visible spectrophotometer of UV1800 shimadzu model. Before analysis, the equipment was verified and calibrated by analyzing a mid-point calibration standard (check) and a calibration blank at the beginning and at end of a sample run and periodically during a run. The check standard confirmed if the instrumental method (calibration) was still fit for purpose once the value obtained was between 90 and 110 % recovery. A quality control external sample and a blank spike was prepared and treated as the samples and analysed to determine the percentage recovery. Duplicate analysis of samples was also performed during analytical procedures to measure precision of the analytical process.

A stock nitrate standard solution (100 mg/L) was prepared by dissolving 0.7218 g of Potassium nitrate in 1000 mL of nitrate free de-ionized water. An Intermediate nitrate standard solution was also prepared by diluting 100 mL of the stock solution to 1000 mL with de-ionised water; 1 mL = 10 $\mu\text{g NO}_3^-$. The solution was preserved by adding 2 mL of CHCl_3 . The calibration curve was then constructed by preparing standards ranging from 0 to 7 ppm.

For sample treatment, 1 mL of 1 N hydrochloric acid solution was added to 50 mL of clear sample and mixed thoroughly. 10 mL of this sample was fed into the UV-visible spectrophotometer and the absorbance of the sample was read at a wavelength of 220 nm to obtain the nitrates reading and at 275 nm to determine absorbance due to dissolved organic matter interferences. For samples and standards, two times the absorbance reading at 275 nm was subtracted from the reading at 220 nm to obtain a reading due to nitrates. The calibration curve was constructed by plotting the absorbance of nitrates against the concentration of nitrate standards and the sample concentrations was obtained directly from the curve.

For ammonia, titrimetric method was used following a preliminary distillation step. The sample was distilled by adding 25 mL of borate buffer solution to 500 ml of the sample in a sample flask and the pH was adjusted to 9.50 by addition of 6 N sodium hydroxide using a pH meter. The sample flask was connected to the distillation apparatus with the tip of the delivery tube below the surface of the acid receiving solution. The distillate was collected at a rate of 6 mL to 10 mL / minute in a 500 mL flask containing 50 mL of indicating boric acid solution which turned bluish green indicating presence of ammonia. 100 mL of the distillate was titrated with a standard 0.02 N sulphuric acid using a mixture of methyl red and methylene blue as an indicator until the solution turned to light pink-red. A blank sample of ammonia free water was also distilled and titrated for correction of the results. Three replicates were done to ensure validity of results. The amount of ammonium nitrogen [$\text{NH}_3\text{-N}(\mu\text{g L}^{-1})$] present in the sample was obtained using the formula below;

$$\text{mg NH}_3\text{-N/L} = \frac{(\text{A-B}) \times 280}{\text{mL sample}}$$

where A = Volume of sulphuric acid titrated for the sample,

B = Volume of sulphuric acid titrated for blank

3.4.3 Testing for heavy metal concentrations

Heavy metals analyzed in tannery effluent samples were Pb, Zn, Ni, Cu, and Cr. These metals were selected based on their health and environmental risk on the people who consume water from their discharge points. Heavy metals were analysed according to standard methods of the American Public Health Association (APHA, 2005). 100 mL of the water samples was measured in duplicates and 5 mL of conc. HNO_3 solution was added in a borosilicate glass beaker, incubated at 80 °C-105 °C in a water bath for digestion for 2 hours. The digested samples were removed from the water bath, allowed to cool and then filtered using filter papers whatman-42, of 0.45 μm to remove any suspended particulate matter. The sample was diluted to 50 mL and analyzed for Trace elements using ICPOE (Inductively coupled plasma optical emissions spectroscopy). All the reagents used were analytical grade.

3.4.4 Preparation of biochar

Green banana peels samples from Kalerwe market and Coffee husks from Kawempe coffee processing machine were thoroughly washed with distilled deionized water and dried in a laboratory oven at 60 °C for 72 hours to a constant weight. The dry material was milled using an electric grinder, sieved to 2.36 mm and stored in air tight plastic self-sealing bags. For modifications, 100g of the material were soaked in 0.25 M NaOH for 2 hours and neutralized using 0.25 M HCl. The modified bio-sorbent was generously washed with distilled water, dried in an oven at 105 °C for 24 hours and stored in plastic bags (Bakyayita et al., 2015). Some portions of the powdered bio-sorbent materials were used for FTIR and Carbonated carbon, Total carbon content, hydrogen index, oxygen index, oil saturation index analyses to cater for characterization of bio sorbent.

3.4.5 Characterization of biochar

The obtained bio-sorbent was characterized for functional groups. Fourier transform infrared (FTIR) experiments were performed with the aid of a Shimadzu FTIR spectrophotometer. The sample pan and the bottom of the pointer of the adjustment knob were cleaned with ethanol and soft tissue, and the sample was held to the position by the knob pointer. The knob was adjusted till a click was felt in the knob. Once the sample was placed in position, the sample scan was clicked on the software window. The spectra were obtained using the technique of ATR (attenuated total reflection) in which the samples were pressed against a ZnSe crystal and collected over a range of 4000–400 cm by averaging 20 scans at a resolution of 4 cm (Figure 1).



Figure 2: The Shimadzu FTIR spectrophotometer was used to identify functional groups.

The biosorbent was also characterized for HI, OI, AI, CC, TOC, and OSI where two analyses were performed with the first being pyrolysis where the organic compounds in the sample were carried by helium from the oven (set at 300 °C and ends at 650 °C) to the flame ionization detector (FID) whose flame is lit by a mixture of hydrogen and air causing the ionization of the organic compounds whose hydrocarbon content was then detected by FID. The oven was then cooled to 300 °C and then the oxidation cycle was initiated to run up to 850 °C where the sample was subjected to air which was also used to transport the oxidation products to two infrared (IR) detectors, one of which detected the CO bonds bandwidth while the second infrared detected the CO₂ bonds bandwidth (Figure 2).

3.4.6 Biosorption experiments

Biosorption experiments with modification have been described by Bakyayita, *et al.*, (2015). 5.0 g of biosorbent was weighed into a 250 mL beaker and 6 mg/L solution of chromium was added. The mixture of the two was transferred into a settling column of diameter 3.2327 cm and given contact time between 20 and 80 minutes. The biosorption studies were done in triplicate at $24 \pm 1^\circ\text{C}$. 50 mL of the effluent was transferred into 50 mL falcon tubes for analysis using an inductively coupled plasma-optical emission (ICP-OE) spectroscopy. The above procedure was repeated for

all the runs. For biochar involving mixing of different biomass wastes lots, they were blended in equal proportions of 2.5 g each to make 5 g used in each run.

3.5 Data analysis

Data on physico-chemical properties and heavy metal concentration of tannery effluent were entered in Microsoft excel 2010 and checked for errors, checked for normal distribution and heterogeneity of variances using the shapiro-wilk test in SPSS software (Version 23). Normality testing aimed at determining whether parametric or non-parametric tests are suitable for the data set. Then physico-chemical and heavy metal data from different sites was summarised to generate descriptive statistics (mean, standard error, standard deviation, range, minimum and maximum values) which were used to generate frequencies, graphs, tables and charts. One-way analysis of variance (ANOVA) was used to determine variation in the tested physico-chemical and heavy metal concentration parameters between the different sites. In addition, a Tukey's HSD post-hoc test (Sokal & Rohlf, 2012) was used to determine which parameter mean concentrations for sites were significantly different from each other. The p-values of less than 0.05 were considered. All heavy metal concentration acquired were compared with Ugandan national standards for effluents provided by National Environment Management Authority (NEMA).

CHAPTER FOUR: RESULTS AND DISCUSSIONS

4.1 Heavy metal concentration in tannery effluent

Among all metals, Chromium (Cr), Nickel (Ni), Lead (Pb) concentrations in the tannery effluent were significantly different among studied sites. Although Cr and Pb concentrations were higher and above national recommendable standards by NEMA at site 3 than at other sites, Nickel (Ni) was far below the national standard (Table 1). All metals at control site were below detectable limits.

Table 1 : Heavy metals concentrations in the selected tannery sites.

Parameter	Mean $\pm$ SD concentration per study site			P-value	Control	NEMA Standards (mg/L)
	Site 1	Site 2	Site 3			
Cr (mg/L)	0.09 $\pm$ 0.18 ^a	0.06 $\pm$ 0.16 ^c	6.13 $\pm$ 0.44 ^b	0.002	BDL	0.1
Ni (mg/L)	0.0001 $\pm$ 0 ^a	0.003 $\pm$ 0 ^c	0.005 $\pm$ 0 ^b	0.032	BDL	0.1
Cu (mg/L)	0.005 $\pm$ 0.01 ^a	0.002 $\pm$ 0 ^a	0.002 $\pm$ 0 ^a	0.307	BDL	2.0
Zn (mg/L)	0.01 $\pm$ 0.02 ^a	0.002 $\pm$ 0 ^a	0.002 $\pm$ 0 ^a	0.840	BDL	5.0
Pb (mg/L)	0.02 $\pm$ 0.02 ^{ab}	0.01 $\pm$ 0 ^c	0.03 $\pm$ 0.02 ^b	0.040	BDL	0.015

Note: Different letters imply statistically significant different at 5% .

The results presented regarding the concentrations of Chromium (Cr), Nickel (Ni), and Lead (Pb) in tannery effluent offer valuable insights that can be discussed and contextualized within existing literature on environmental pollution, tannery wastewater management, and heavy metal contamination. Numerous studies have documented the detrimental effects of tannery effluent on aquatic ecosystems and human health due to its high content of heavy metals and other pollutants (Tadesse & Guya, 2017). The findings of elevated concentrations of Cr, Ni, and Pb at sites 3 and 1 align with the observations of (Semanda et al., 2018) highlighting the significant contribution of tannery operations to heavy metal pollution in water bodies.

The exceeding of national recommendable standards for Cr (6.13 $\pm$ 0.44 mg/L) and Pb (0.02 $\pm$ 0.02 mg/L) concentrations at site 3 and Pb (0.03 $\pm$ 0.02 mg/L) at site 1 raises concerns about potential health risks to both environmental organisms and communities living in the vicinity. This finding underscores the importance of stringent regulatory measures and effective enforcement to prevent

adverse health effects associated with exposure to heavy metals in contaminated water sources (Baguma et al., 2023).

The spatial variability observed in heavy metal concentrations among the studied tannery sites reflects the heterogeneous nature of pollution sources and environmental factors influencing contaminant transport and fate. Understanding the spatial distribution of contamination can inform targeted remediation strategies and prioritize areas for environmental monitoring and intervention (Zhou & Wang, 2019). The discrepancy in heavy metal concentrations across tannery sites reflect the variations in wastewater treatment practices and the efficacy of pollution control technologies employed by different facilities (Zhou et al., 2020). Comparative assessments of treatment processes and their effectiveness in reducing heavy metal discharge could provide valuable insights for optimizing tannery wastewater management practices (Abate et al., 2020).

Results further revealed Cr accumulation at the tannery effluent discharge point (Figure 3), assumes a certain pattern based on typical industry practices and prior knowledge. However, the observed trend, reveals noteworthy discrepancies from these expectations. Cr trend would align with established industry norms, indicating controlled and consistent levels of chromium. Contrary to, the observed trend presents a departure from the anticipated pattern. The study highlights instances where tanneries, including Site 1 and Site 2, implement waste treatment and recycling measures. Despite these efforts, there is a considerable discharge of chromium into nearby waters, though below permissible levels as per NEMA effluent discharge standards. Such could be attributed to treatment processes, such as precipitation using Magnesium oxide, tree planting projects, and sedimentation ponds.

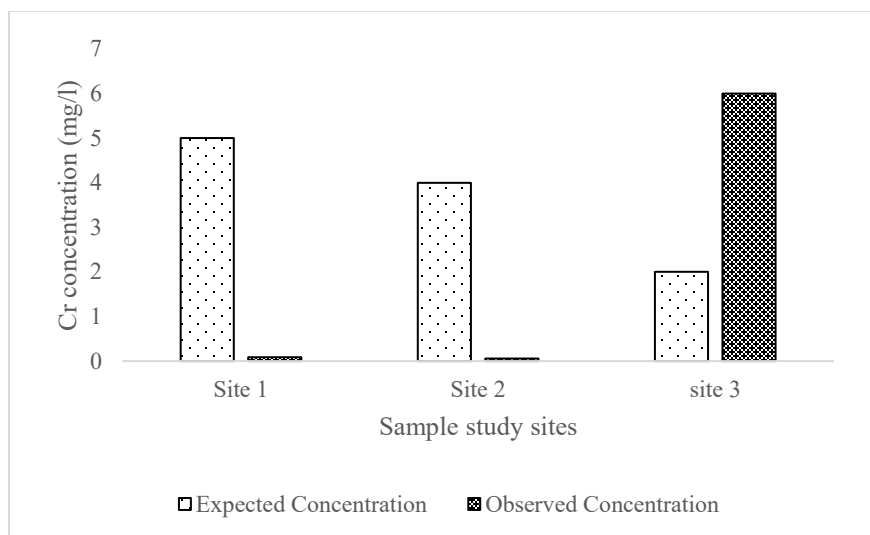


Figure 3: Expected vs observed trends of chromium accumulation in water at tannery effluent discharge point.

The discrepancy between expected and observed trends of chromium (Cr) accumulation at the tannery effluent discharge point, as depicted in Figure 3, presents an intriguing deviation from conventional industry practices and prior knowledge. This finding invites a nuanced discussion within the context of existing literature on tannery wastewater management and heavy metal contamination.

Historically, tanneries have been associated with significant chromium pollution due to the use of chromium-based compounds in leather tanning processes (Bilal & Kumar, 2023). However, in recent years, regulatory measures and industry initiatives have aimed to mitigate environmental impacts through the adoption of waste treatment and recycling technologies (Perkumienė et al., 2023). The expected trend of controlled and consistent levels of chromium at the discharge point aligns with efforts to comply with permissible limits set by environmental regulations (Younas et al., 2023).

The observed departure from the anticipated pattern suggests operational challenges or inadequacies in waste treatment practices at the studied tanneries (Mohammed, 2017). Despite implementing treatment measures such as precipitation using Magnesium oxide, tree planting projects, and sedimentation ponds, there remains a notable discharge of chromium into nearby waters (Minas et al., 2017). This discrepancy underscores the complexity of tannery wastewater

management and highlights the need for continuous monitoring and improvement of treatment processes (Bwapwa et al., 2024).

The findings raise questions about the effectiveness of specific treatment technologies in removing chromium from tannery effluent (Nur-E-Alam et al., 2020). While treatment methods like precipitation and sedimentation are commonly used for heavy metal removal, their efficacy can vary depending on factors such as pH, temperature, and the presence of other contaminants (Qasem et al., 2021). Further investigation into the performance of these treatment processes and potential optimization strategies is warranted to enhance chromium removal efficiency.

The positive influence of the pH and Temperature in influencing the biochar effectiveness as an adsorbent by impacting the surface chemistry of the biochar and enhance or hinder the mobility of the contaminants in the solution cannot be ignored (Wang et al., 2025).

The study's findings have implications for environmental sustainability and ecosystem health in tannery-affected areas. Despite chromium levels being below permissible limits, the discharge of even trace amounts of this heavy metal into water bodies can have adverse effects on aquatic organisms and ecosystems (Aziz et al., 2023). Addressing the root causes of chromium contamination and exploring innovative approaches to wastewater treatment are essential for minimizing environmental impacts and ensuring long-term sustainability.

4.2 Toxicity of tannery effluent from selected sites

Tannery effluent from selected sites was tested for quality in comparison to surface water picked from River Nile (Control site) and the national standard values (Table 2). Water physico-chemical characteristics and nutrient concentrations from samples at different sampling sites had significantly different ($P \leq 0.05$) concentrations. All parameters considered varied significantly ($P < 0.05$) among sampled sites (Table 2). The pH among sites ranged from 4.83 at site 3 to 9.80 at site 1. Turbidity was least at the control site and highest at site 3. Highest EC was registered at site 3 and least at the control site. Site 3 further had the highest Total dissolved solids, Total suspended solids, Sulphates, Nitrates, Ammonium, Total Nitrogen, BOD, and COD whereas it had the lowest Total phosphorous, pH, reactive phosphorous and chloride (Table 2). Site 1 and 2 had similar concentrations of the different studied elements

Table 2: Toxicity of tannery effluent collected at selected sites in Uganda.

Variable	Mean $\pm$ SD concentration per study site				NEMA Standard values
	Site 1	Site 2	Site 3	Control	
Turbidity	268.67 $\pm$ 1.15 ^b	268.67 $\pm$ 1.15 ^b	1107.67 $\pm$ 12.42 ^a	7.67 $\pm$ 0.06 ^c	25
pH (pH units)	9.80 $\pm$ 0.00 ^a	9.80 $\pm$ 0.00 ^a	4.83 $\pm$ 0.06 ^c	7.00 $\pm$ 0.00 ^b	5.0-8.5
Electrical Conductivity (μ S/cm)	5890.00 $\pm$ 34.64 ^b	5890.00 $\pm$ 34.64 ^b	11724.00 $\pm$ 12.17 ^a	160.67 $\pm$ 3.06 ^c	1000
Total Dissolved Solids (mg/L)	4123.00 $\pm$ 24.25 ^{ab}	4123.00 $\pm$ 24.25 ^{ab}	5474.33 $\pm$ 4740.91 ^a	112.33 $\pm$ 2.52 ^b	750
Sulphates(mg/L)	136.67 $\pm$ 11.55 ^b	136.67 $\pm$ 11.55 ^b	336.67 $\pm$ 2.89 ^a	10.33 $\pm$ 1.53 ^c	500
Chloride(mg/L)	1600.00 $\pm$ 0.00 ^a	1600.00 $\pm$ 0.00 ^a	402.00 $\pm$ 0.00 ^b	13.67 $\pm$ 1.15 ^c	250
Reactive Phosphorus-P (mg/L)	4.90 $\pm$ 0.00 ^a	4.90 $\pm$ 0.00 ^a	0.45 $\pm$ 0.02 ^b	0.04 $\pm$ 0.01 ^c	5
Nitrates-N(mg/L)	0.13 $\pm$ 0.06 ^b	0.13 $\pm$ 0.06 ^b	0.63 $\pm$ 0.12 ^a	0.17 $\pm$ 0.03 ^b	10
Ammonium-N(mg/L)	0.003 $\pm$ 0.001 ^c	0.003 $\pm$ 0.001 ^c	0.380 $\pm$ 0.017 ^b	1.327 $\pm$ 0.103 ^a	10
Total Nitrogen(mg/L)	0.17 $\pm$ 0.07 ^b	0.17 $\pm$ 0.07 ^c	1.25 $\pm$ 0.15 ^c	1.84 $\pm$ 0.13 ^a	10
Total Phosphorus(mg/L)	6.14 $\pm$ 0.01 ^a	6.14 $\pm$ 0.01 ^a	0.57 $\pm$ 0.03 ^b	0.05 $\pm$ 0.01 ^c	5
Biological Oxygen Demand (mg/L)	1100.00 $\pm$ 0.00 ^b	1100.00 $\pm$ 0.00 ^b	1604.00 $\pm$ 5.29 ^a	13.67 $\pm$ 1.15 ^c	50
Chemical Oxygen Demand (mg/L)	2216.67 $\pm$ 5.77 ^b	2216.67 $\pm$ 5.77 ^b	3470.67 $\pm$ 10.07 ^a	419.33 $\pm$ 9.02 ^c	70
Total Suspended Solids (mg/L)	558.33 $\pm$ 2.89 ^b	558.33 $\pm$ 2.89 ^b	1839.67 $\pm$ 2.52 ^a	27.33 $\pm$ 2.52 ^c	50

Note: Different letters imply statistically significant different at 5%

The toxicity of tannery effluent is evidenced by the results from the selected sites in the study. The significant variations in physico-chemical characteristics and nutrient concentrations among sampled sites indicate potential ecological risks associated with tannery effluent discharge, as highlighted below:

High turbidity and TSS levels, particularly observed at site 3, are indicative of suspended solids and organic matter in the water column. Previous studies have demonstrated that elevated turbidity and TSS can impair light penetration, disrupt aquatic habitats, and hinder the growth and reproduction of aquatic organisms (Bilotta & Brazier, 2008).

Elevated EC and TDS levels, as observed at site 3, suggest increased salinity and dissolved mineral content in the water (Ghalib, 2017). Tannery effluent often contains high concentrations of salts and heavy metals, which can adversely affect aquatic organisms by disrupting osmoregulation and physiological processes (Singh et al., 2023).

Elevated concentrations of sulphates, chloride, nitrates, phosphorus, and nitrogen, particularly at site 3, indicate nutrient enrichment and potential eutrophication of receiving water bodies (Akinnowo, 2023). Previous research has shown that excessive nutrient loading from tannery effluent can stimulate algal growth, leading to oxygen depletion, fish kills, and the degradation of aquatic ecosystems (Suresh et al., 2023).

High BOD and COD levels, particularly observed at site 3, signify organic pollution and oxygen demand in the water (Vigiak et al., 2019). Tannery effluent contains organic compounds such as proteins, fats, and tannins, which can undergo microbial decomposition, consuming dissolved oxygen and creating hypoxic conditions detrimental to aquatic life (Mwinyihija et al., 2006).

4.3 Biochar characterization using Green banana peels and Coffee husks

4.3.1 Hawk pyrolysis characterization of biochar

To better understand the characterization of biochar, a hawk pyrolysis was adopted, here different biochar types that included treated banana peels, treated coffee husks, a combination of treated banana peels and treated coffee husks, non-treated banana peels, non-treated coffee husks and a combination of non-treated banana peels and non-treated coffee husks were used. Study results showed non-treated coffee husks with highest value of total organic carbon (36.76 wt.%), oxygen index (156), carbonated carbon (1.69 wt.%), however, it also possessed the lowest hydrogen index (291) and saturation index value (94) per gram sample. Treated banana peel biochar had the least total organic carbon (33.25 wt.%), and oxygen index (70). In addition, the combination of non-treated coffee husks and non-treated banana peel biochar had the least carbonated carbon, hydrogen index, and a relatively low oxygen index and total organic carbon (Table 3).

Table 3: Biochar characterization using the hawk pyrolysis machine

Biochar	TOC (wt. %)	HI	OI	CC (wt. %)	OSI
T.B.P	33.25	313	70	0.65	243
T.C.H	36.07	340	74	0.81	89
T.C.H + T.B.P	33.79	291	73	0.71	189
N.T.C.H	36.76	291	156	1.69	94
N.T.B.P	34.35	312	81	0.44	184
N.T.C.H +N.T.B.P	33.29	291	74	0.41	221

The relationship between the proportion removed and the pyrolysis parameter were analyzed. It was observed that, there was a positive relationship between total organic carbon (TOC) and the removed percentage with a coefficient of 0.19, also Hydrogen index (HI) and the removed the correlation was positive with coefficient of 0.01. The same positive relation was observed for oxygen index (OI) with a correlation coefficient of 0.17 and then carbonated carbon (CC) with a correlation coefficient of 0.19 with what was removed. The observed positive coefficient between the removed percentage with TOC, HI, OI and CC implied that as the pyrolysis parameters increased, the percentage removed also increased. Though this was slow for HI since it had the weakest correlation coefficient of 0.01 and a bit faster for TOC, CC and OI. For free oils (OSI) and the removal percentage the relation was negative that a correlation coefficient of -0.17 which implied that as OSI, increased, the removed percentage dropped (Table 4).

Table 4:Correlation between the proportion removed and the pyrolysis parameter

Hawk pyrolysis parameter	Percentage removal correlation
TOC	0.19
HI	0.01
OI	0.17
CC	0.19
OSI	-0.17

The results from the hawk pyrolysis characterization of different biochar types provide valuable insights into their properties and absorption capacities, which can be interpreted in the context of previous literature on biochar production and application. Here's a discussion highlighting the relationship between hawk pyrolysis parameters and absorption capacities:

The positive relationship between TOC and the percentage removed suggests that biochar with higher TOC content exhibit greater absorption capacities. This finding aligns with previous studies that have demonstrated the importance of carbonaceous materials in adsorbing organic contaminants from water and soil environments (Scaria et al., 2022).

Although the correlation coefficient for HI is low, the positive relationship implies that higher HI values correspond to increased absorption capacities, albeit to a lesser extent compared to TOC. Previous research has indicated that hydrogen-rich biochar may have enhanced sorption capabilities for certain contaminants due to the presence of functional groups such as hydroxyl and amino groups (Kapoor & Zdarta, 2024).

The positive correlations between OI, CC, and the percentage removed suggest that biochar with higher oxygen content and carbonation exhibit improved adsorption efficiency. Oxygen-containing functional groups on biochar surfaces can facilitate interactions with polar contaminants through hydrogen bonding and π - π electron interactions, enhancing sorption capacity (Yu et al., 2021).

The negative correlation between OSI and the percentage removed indicates that biochar with lower free oil content demonstrate higher absorption capacities. This finding is consistent with the notion that free oils may hinder the accessibility of sorption sites on biochar surfaces, thereby reducing their effectiveness in adsorbing contaminants (Haider et al., 2022).

4.3.2 FTIR characterization of biochar

FTIR characterizes the biochar used along eight FTIR peaks. Generally, the untreated banana peels and untreated coffee husks had better adsorption characteristics such as Aliphatic C-H stretching, Aldehyde C-H stretching, Aliphatic acid C=O stretching, Unsaturated group like alkene, Si-O stretching and aromatic C-NO₂ stretching. However, the treated coffee husk biochar was better at surface O-H stretching and carboxylate anion C=O stretching. On the other hand, the untreated banana peel biochar was lowest absorption of unsaturated group like alkene, carboxylate anion C=O stretching and aromatic C-NO₂ stretching. The treated banana peel biochar had the least absorption characteristics over the five peaks such as surface O-H stretching, Aliphatic C-H stretching, Aldehyde C-H stretching, and Si-O stretching. (Table 5).

Table 5: FTIR characterization of the biochar

S/No	Compounds	BANANA PEELS		COFFEE HUSKS	
		UN TREATED	TREATED	UN TREATED	TREATED
1	Surface O-H stretching	3335	3300	3362	3326.74
2	Aliphatic C-H stretching	2930.94	2922.49	2930.94	2922.49
3	Aldehyde C-H stretching	2860.23	2851.78	2860.23	2860.23
4	Aliphatic acid C=O stretching	1760.43	1734.3	1734.3	1742.75
5	Unsaturated group like alkene	1637.46	1655.14	1655.14	1645.92
6	Carboxylate anion C=O stretching	1356.17	1364.62	1364.62	1373.08
7	Si-O stretching	1030.3	1004.17	1030.3	1012.63
8	Aromatic C-NO ₂ Stretching	1426.11	1461.46	1469.92	1453.01

Further to understudy the relationship between the stretching and the percentage removal a correlation analysis was used. Here a positive relationship was observed between Surface O-H stretching, Aliphatic C-H stretching, Aldehyde C-H stretching, Unsaturated group like alkene, Carboxylate anion C=O stretching, Si-O stretching, and Aromatic C-NO₂ Stretching with the percentage removed. The implication here was that as the stretching bonds increased, the higher the percentage removed. Though this was least for Aliphatic C-H stretching, Unsaturated group like alkene and Carboxylate Anion C=O stretching with the percentage removal with correlation coefficients of 0.09, 0.07, and 0.06 respectively. Whereas the relationship between Aliphatic acid C=O stretching and the removal percentage was negative with a correlation coefficient of -0.08 which implied that the removal percentage dropped as Aliphatic acid C=O stretching increased (Table 6).

Table 6: Correlation between stretching bonds and percentage removed

Stretching bonds	Removal Percentage correlation
Surface O-H stretching	0.17
Aliphatic C-H stretching	0.09
Aldehyde C-H stretching	0.12
Aliphatic acid C=O stretching	-0.08
Unsaturated group like alkene	0.07
Carboxylate anion C=O stretching	0.06
Si-O stretching	0.11
Aromatic C-NO ₂ Stretching	0.11

The FTIR characterization of biochar provided valuable insights into the functional groups present in the materials, shedding light on their potential adsorption characteristics. Here's a discussion of the relationship between FTIR peaks and the percentage removal of contaminants, drawing on the results presented in Table 5 and Table 6, along with insights from previous literature:

The positive correlation between surface O-H stretching and the percentage removal suggests that biochars with higher surface hydroxyl groups exhibit greater adsorption capacities (Zhu et al., 2023). Hydroxyl groups on biochar surfaces can participate in hydrogen bonding with contaminants, facilitating their removal from aqueous solutions (Dong et al., 2024). Previous studies have highlighted the importance of surface hydroxyl groups in enhancing the adsorption of polar compounds such as heavy metals and organic pollutants (Bao et al., 2021).

The positive correlations observed for aliphatic C-H and aldehyde C-H stretching indicate that biochars with higher concentrations of these functional groups tend to exhibit better adsorption capabilities (Trazzi et al., 2024). Aliphatic and aldehyde groups can contribute to the formation of π - π electron interactions and van der Waals forces, enhancing the sorption of hydrophobic contaminants (Fu et al., 2021). Previous research has demonstrated the role of aliphatic and aldehyde functional groups in facilitating the adsorption of organic pollutants onto biochar surfaces (Yang et al., 2022).

The negative correlation between aliphatic acid C=O stretching and the percentage removal suggests an inverse relationship between this functional group and adsorption capacity (Bibi et al., 2023). Aliphatic acid groups may compete with contaminants for sorption sites on biochar surfaces, leading to reduced removal efficiencies (Yang, et al., 2022). Previous studies have reported that carboxylic acid groups can act as competitive adsorption sites for certain contaminants, thereby diminishing the overall adsorption capacity of biochar materials (Dong et al., 2024).

The positive correlations observed for unsaturated group like alkene and carboxylate anion C=O stretching suggest their potential contribution to adsorption capacity, albeit with weaker correlations compared to other functional groups (Torrissi et al., 2010). Unsaturated groups and

carboxylate anions may participate in π - π electron interactions and electrostatic interactions, respectively, influencing the adsorption behavior of biochar materials (Ambaye et al., 2020).

The positive correlations for Si-O stretching and aromatic C-NO₂ stretching indicate their potential role in enhancing adsorption capacities. Si-O bonds in biochar structures can contribute to surface area and porosity (Taherymoosavi et al., 2017), while aromatic groups can facilitate π - π electron interactions with aromatic contaminants (Zhu et al., 2004). Previous studies have highlighted the importance of these functional groups in governing the adsorption behavior of biochar materials (Gryta et al., 2023).

4.3.2.1 Coffee husks biochar

The composition of functional groups in coffee husks biochar was elucidated through distinct peaks. The broad band at 3250 cm⁻¹ signified presence of O-H (hydroxyl) surface groups, indicative of surface reactivity and water adsorption. A notable peak at 1640 cm⁻¹ suggested the existence of C=O (carbonyl) groups, possibly originating from ketones or aldehydes. The peak at 1100 cm⁻¹ corresponded to the C-O stretching in the polysaccharide carbohydrate region, implying the presence of carbohydrates, potentially in the form of polysaccharides, within the biochar structure. Additionally, a weaker band at 2800 cm⁻¹ points to C-H (carbon-hydrogen) groups, characteristic of organic compounds suggested an aliphatic hydrocarbon component (Figure 4). While the biochar samples share common functional groups, differences in peak intensities signify variations in the abundance or structural arrangement of these groups among different samples.

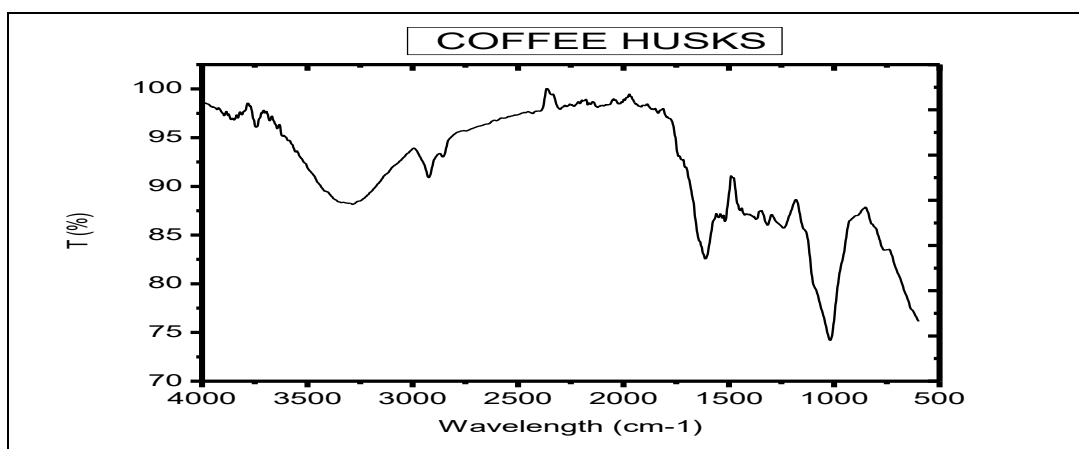


Figure 4: The Transmission spectrum for the untreated coffee husks biochar.

4.3.2.2 Treated coffee husks biochar

The band around 3250 cm^{-1} in Figure 5 indicates the presence of O-H surface groups, characteristic of hydroxyl functional groups. Similarly, the peak at 1640 cm^{-1} implies the presence of a C=O group, likely associated with carbonyl functional groups, suggesting surface reactivity and water adsorption capabilities. Additionally, the peak at 1100 cm^{-1} is attributed to the C-O polysaccharide carbohydrate region, indicating the presence of carbohydrates, potentially in the form of polysaccharides.

Notably, when assessing shape variations between treated and untreated coffee husks biochar, Figure 5 reveals an introduction of a weak band at 2800 cm^{-1} . This band is indicative of C-H stretching, suggesting the presence of aliphatic hydrocarbons. The emergence of this additional band suggests alterations in the chemical composition, likely resulting from the treatment process applied to the coffee husks. While the main functional groups remain consistent with untreated biochar, the presence of new peaks indicates modifications that may impact the reactivity and adsorption capacity of the treated coffee husks biochar.

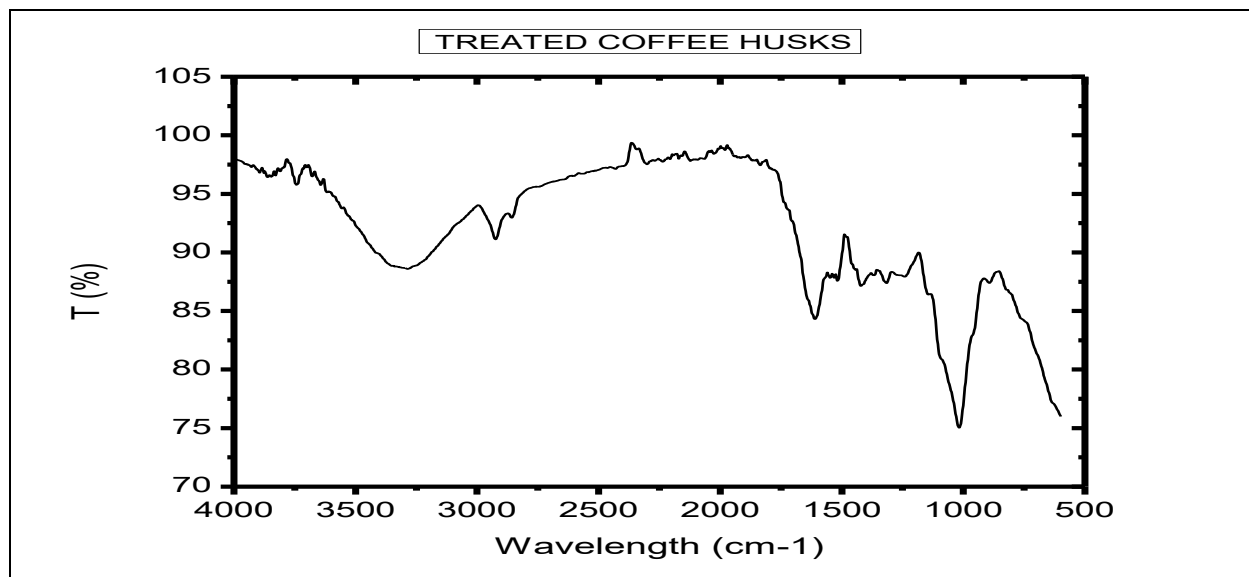


Figure 5: The Transmission spectrum for the treated coffee husks biochar.

The FTIR analysis revealed the presence of O-H surface groups, C=O carbonyl groups, polysaccharides, and aliphatic hydrocarbons in the Untreated Coffee Husks Biochar. These

functional groups contribute to its surface reactivity and adsorption potential. Similar functional groups were identified in treated biochar, including O-H and C=O groups. Additionally, a weak band at 2800 cm^{-1} indicated the presence of additional C-H stretching, suggesting the introduction of aliphatic hydrocarbons. The presence of these additional functional groups can enhance its adsorption properties compared to untreated biochar. The differences in the chemical composition of untreated and treated coffee husks biochar can be attributed to the treatment process applied to the raw material.

Pyrolysis, the process of heating organic material in the absence of oxygen, is used to produce biochar (Basu, 2018). The temperature, heating rate, and duration of pyrolysis can influence the chemical composition and properties of the resulting biochar (Tomczyk et al., 2020). Differences in pyrolysis conditions between untreated and treated coffee husks biochar leads to variations in their chemical composition (Xing et al., 2021).

Treated coffee husks biochar undergoes additional chemical treatments or modifications beyond standard pyrolysis (Díaz et al., 2024). These treatments involve the use of acids, bases, or other chemicals to alter the surface chemistry and functional groups of the biochar (Yao & Zhou, 2022). For example, acid treatment removes ash content and increase surface area, while alkaline treatment may introduce new functional groups or modify existing ones (Feng et al., 2013).

The treatment process applied to coffee husks biochar involves the removal of impurities, such as ash, metals, and organic contaminants (Kapoor & Zdarta, 2024). This purification step can result in differences in the chemical composition and purity of untreated and treated biochar (Shahib et al., 2022). Removal of impurities can enhance the surface reactivity and adsorption capacity of the treated biochar (Ambaye et al., 2020).

Chemical treatment can introduce or modify functional groups on the surface of biochar, leading to changes in its chemical composition (Tomczyk et al., 2022). For example, treatment with oxidizing agents can increase the abundance of oxygen-containing functional groups, such as carbonyl and carboxyl groups, which enhance the biochar's reactivity and adsorption properties (Dong et al., 2024).

Treatment processes can also alter the surface area, pore structure, and surface morphology of biochar (Yaashikaa & Kumar, 2020). Changes in surface area and porosity influence the biochar's adsorption capacity by affecting the availability of active sites for contaminant sorption (Jagadeesh & Sundaram, 2023). Treatment can increase surface area and pore volume, thereby enhancing the adsorption efficiency of the biochar (Wu et al., 2024).

The chemical composition of the raw material (coffee husks) can also impact the resulting biochar composition (Kiggundu & Sittamukyoto, 2019). Variations in the feedstock composition, such as moisture content, lignin, cellulose, and hemicellulose content, can lead to differences in the chemical composition and properties of untreated and treated coffee husks biochar (Rangabhashiyam & Balasubramanian, 2019).

The differences observed in the chemical composition of untreated and treated coffee husks biochar have implications for their effectiveness as adsorbents (Oliveira et al., 2008). Treated biochar can offer improved adsorption efficiency due to the presence of additional functional groups introduced during the treatment process (Jagadeesh & Sundaram, 2023).

4.3.2.3 Banana peels biochar

In Figure 6, the functional group composition of banana peels biochar is unveiled through characteristic peaks. A broad peak at 3250 cm^{-1} is attributed to the hydroxyl functional group, indicating surface reactivity and water adsorption. A sharp bond at 2900 cm^{-1} signifies O-H stretching of amino acid groups, suggesting the presence of amino acids within the biochar structure. At 17120 cm^{-1} , a peak denotes the presence of aliphatic ketones, specifically the C=O stretch.

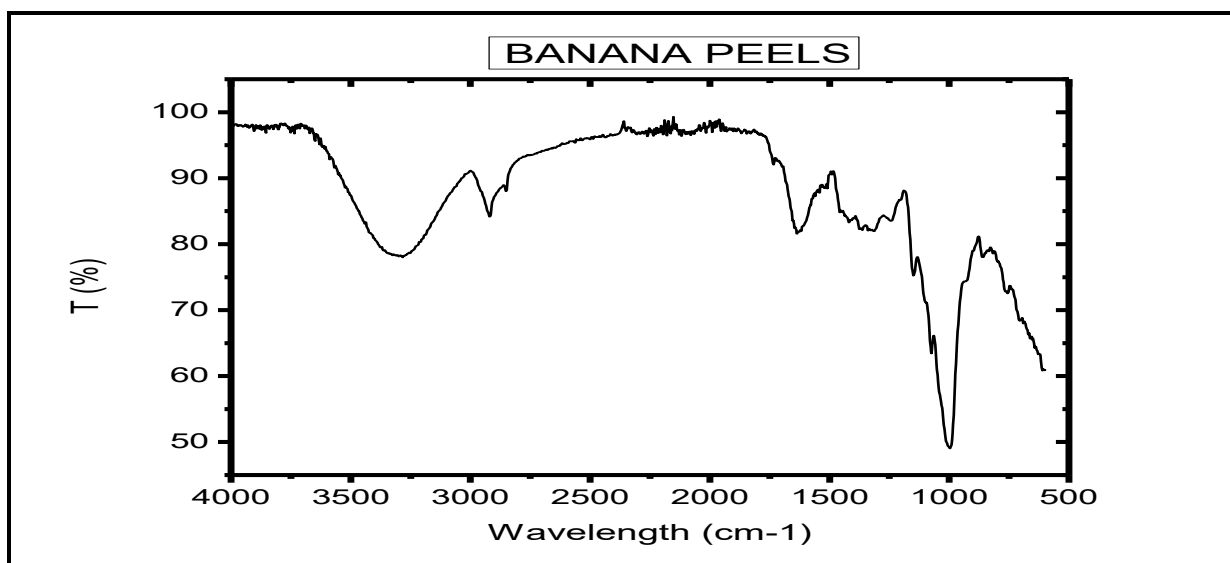


Figure 6: The transmission spectrum for the untreated banana peels biochar.

4.3.2.4 Treated banana peels biochar

Figure 7 presents the composition of functional groups in treated banana peels biochar. The broad peak at 3250 cm^{-1} is indicative of the presence of hydroxyl functional groups, contributing to surface reactivity and water adsorption capabilities. Additionally, a bond between 2800 cm^{-1} and 3000 cm^{-1} is observed, suggesting C-H stretching in alkanes and implying the presence of aliphatic hydrocarbons within the treated banana peels biochar. Notably, the treated banana peels biochar displays a distinctive peak at 1710 cm^{-1} , corresponding to the C=O vibrations of carboxylic groups. This peak implies the introduction or enhancement of carboxyl functional groups as a result of the treatment process. The presence of these additional functional groups indicates chemical modifications during treatment, contributing to potential alterations in the biochar's reactivity.

Comparatively, the functional group composition of treated banana peels biochar, as described in Figure 7, shares similarities with untreated banana peels biochar, particularly in the presence of hydroxyl groups. However, differences in additional functional groups and peak characteristics underscore the impact of the treatment process on modifying the biochar's chemical composition.

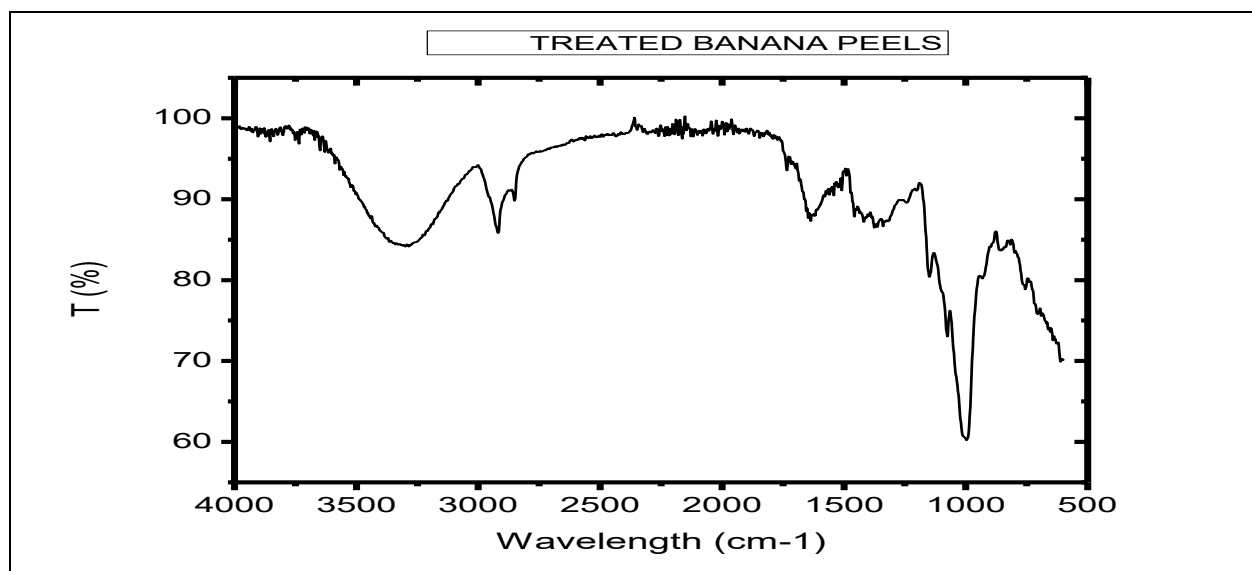


Figure 7: The transmission spectrum for the treated banana peels biochar.

The FTIR analysis revealed the presence of hydroxyl functional groups (broad peak at 3250 cm^{-1}), amino acid groups (sharp peak at 2900 cm^{-1}), and aliphatic ketones (peak at 1712 cm^{-1}) in untreated banana peels biochar. Hydroxyl functional groups contribute to surface reactivity and water adsorption capabilities (Fatima et al., 2019). Amino acid groups provide additional binding sites for specific contaminants, enhancing the biochar's selectivity and adsorption efficiency (Chen et al., 2019). Aliphatic ketones can also participate in interactions with contaminants, potentially increasing the biochar's adsorption capacity (Yang et al., 2016).

Similar functional groups were identified in treated banana peels biochar, including hydroxyl groups (broad peak at 3250 cm^{-1}) and aliphatic hydrocarbons (bond between 2800 cm^{-1} and 3000 cm^{-1}). Additionally, a distinctive peak at 1710 cm^{-1} suggests the presence of carboxylic groups (C=O vibrations), indicating chemical modifications during the treatment process (Bhattacharya & Chaudhari, 2014). The presence of hydroxyl groups contributes to surface reactivity and water adsorption capabilities, similar to untreated biochar. Aliphatic hydrocarbons enhance the biochar's hydrophobicity and affinity for nonpolar contaminants (Fu et al., 2018). The introduction or enhancement of carboxylic groups through treatment can increase the biochar's acidity and provide additional binding sites for charged contaminants, thereby enhancing its adsorption capacity (Luo et al., 2023).

Both untreated and treated banana peels biochar exhibit hydroxyl functional groups, which play a crucial role in surface reactivity and water adsorption. However, treated biochar displays additional functional groups, such as aliphatic hydrocarbons and carboxylic groups, resulting from chemical modifications during treatment. The presence of these additional functional groups in treated biochar may enhance its adsorption capacities by providing additional binding sites, increasing surface reactivity, and altering the biochar's chemical properties.

Previous studies have demonstrated the significance of hydroxyl groups in enhancing the adsorption capacities of biochar by providing active sites for contaminant sorption (Wang et al., 2020). Additionally, the introduction of carboxylic groups through chemical modifications has been shown to increase the biochar's adsorption efficiency for charged contaminants (Murtaza et al., 2024).

4.3.2.5 The banana peels and coffee husks biochar

In Figure 8, the broad band around 3250 cm^{-1} signifies the presence of O-H surface groups, indicating hydroxyl functional groups. The weak peak at 1640 cm^{-1} suggests the existence of a C=O group, likely associated with carbonyl functional groups. Furthermore, the peak at 1100 cm^{-1} is attributed to the C-O polysaccharide carbohydrate region, indicating the presence of carbohydrates, potentially in the form of polysaccharides. This suggests the presence of aliphatic hydrocarbons, possibly introduced or enhanced by the combination of coffee husks and banana peels in the biochar. The simultaneous presence of functional groups characteristic of both coffee husks and banana peels highlights the combined composition resulting from the biocharization process. The shape variations observed in Figure 8 compared to individual biochars signifies the synergistic interactions between the coffee husks and banana peels during the biocharization process.

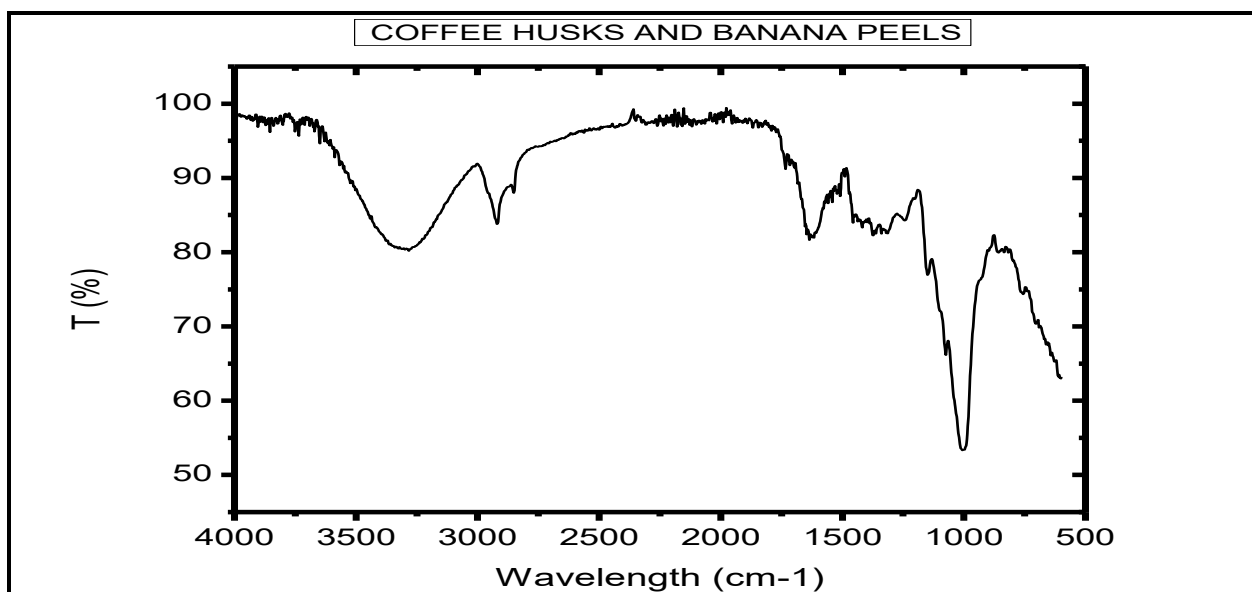


Figure 8: The transmission spectrum for the untreated coffee husks and banana peels biochar.

4.3.2.6 The treated banana peels and coffee husks biochar

In Figure 9, the broad band around 3250 cm^{-1} indicates the presence of O-H surface groups, representative of hydroxyl functional groups. The peak at 1640 cm^{-1} suggests the existence of a C=O group, likely associated with carbonyl functional groups. Furthermore, the peak at 1100 cm^{-1} is attributed to the C-O polysaccharide carbohydrate region, indicating the presence of carbohydrates, potentially in the form of polysaccharides. Of significance is the weak band at 2800 cm^{-1} , indicative of C-H stretching. This suggests the presence of aliphatic hydrocarbons, potentially introduced or enhanced during the treatment process applied to the combination of coffee husks and banana peels. The simultaneous presence of functional groups characteristic of both treated coffee husks and banana peels underscores the unique composition resulting from the biocharization process. The observations in Figure 9 provide insights into the impact of the treatment process on the combined biochar from coffee husks and banana peels. The shape variations and intensity of peaks reveal the altered composition, potentially influencing the biochar's reactivity and suitability for environmental applications, such as adsorption and remediation processes.

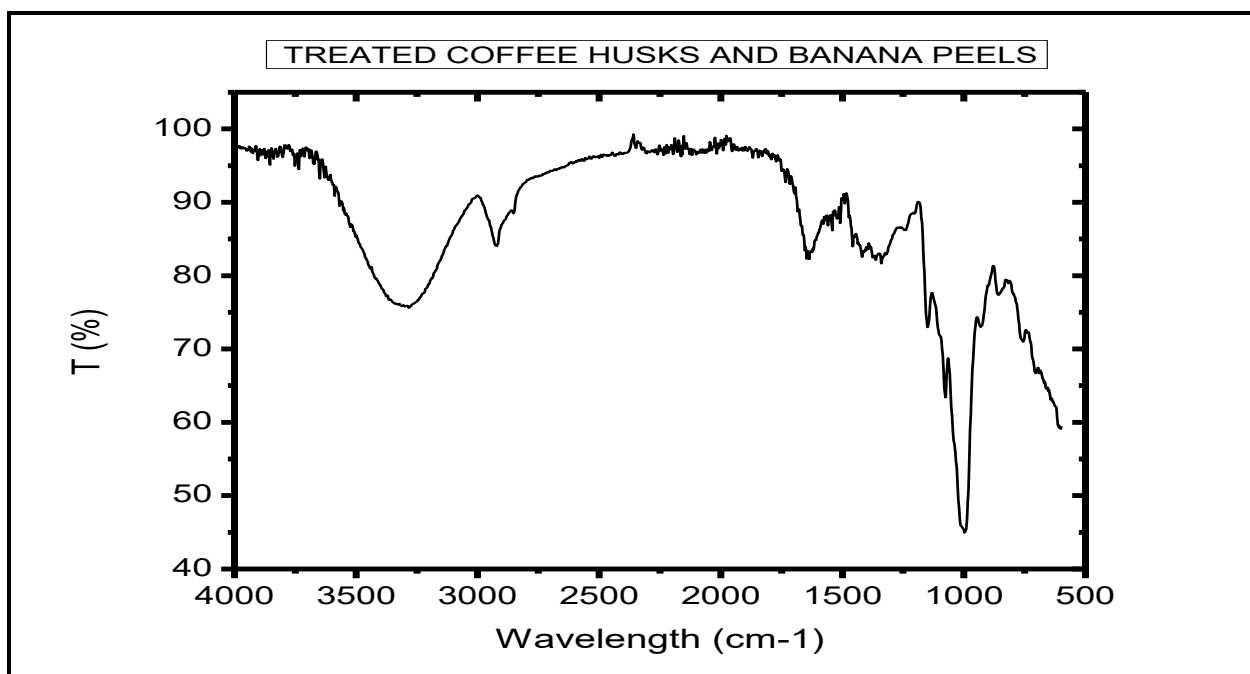


Figure 9: The Transmission spectrum for the treated coffee husks and banana peels biochar.

The FTIR analysis unveiled the presence of key functional groups in both untreated and treated biochar derived from the combination of coffee husks and banana peels. These functional groups include hydroxyl (O-H) surface groups, carbonyl (C=O) groups, and polysaccharides (C-O stretching), which are characteristic of biomass-derived materials (He et al., 2023).

Existing literature on biochar characterization has extensively discussed the significance of these functional groups in influencing the surface chemistry and adsorption properties of biochar (Janu et al., 2021). Hydroxyl groups are known to enhance the surface reactivity and water adsorption capabilities of biochar, while carbonyl groups play a crucial role in its adsorption efficiency for specific contaminants ((Dong et al., 2024; Ambaye et al., 2020).

The observed shape variations in the FTIR spectra compared to individual biochar suggest synergistic interactions between coffee husks and banana peels during the biocharization process. These interactions can lead to the formation of new functional groups or alterations in the abundance and arrangement of existing functional groups within the combined biochar (Ndung'u, 2019).

Previous studies have investigated the impact of feedstock combinations on the chemical composition and properties of biochar. Research by Kwon et al. (2022) demonstrated that blending different biomass feedstocks can result in synergistic effects, leading to enhanced surface area, pore structure, and functional group content in the resulting biochar.

Scholars have extensively studied the influence of functional groups on the adsorption capacities of biochar for various contaminants. For instance, research by Phiri et al. (2024) highlighted the crucial role of hydroxyl groups in enhancing the adsorption efficiency of biochar for heavy metals, pesticides, and organic pollutants.

Additionally, studies by Srivatsav et al. (2020) and Wang et al. (2024) have explored the impact of carbonyl groups on the adsorption properties of biochar, particularly for organic contaminants and dyes. These studies underscore the importance of understanding the chemical composition and surface chemistry of biochar in designing effective adsorbents for environmental remediation.

The findings provide insights into the composition and properties of biochar derived from the combination of coffee husks and banana peels, suggesting its potential suitability for environmental applications such as water and soil remediation. By elucidating the presence and role of functional groups in the combined biochar, the study contributes to the ongoing efforts to develop sustainable and effective adsorbents for mitigating environmental pollution and improving soil fertility.

4.4 Effectiveness of selected natural bio-sorbents in removing heavy metal ions from tannery effluents

4.4.1 Properties and potential adsorption capacities of bio-sorbent

In the characterization of biochar presented in Figure 3, a comprehensive analysis of various parameters across different biochar types provides insights into their properties and potential adsorption capacities. Notably, all biochar samples exhibit a significantly high Hydrogen Index (HI), with the non-treated coffee husks and banana peels mixture showing the highest HI, followed by treated coffee husks and banana peels. Higher HI values generally suggest lower adsorption capacity, indicating a limited relationship. There was an inverse relationship between Oil Saturation Index (OSI) with adsorption capacity. Higher values of OSI and HI suggest lower

adsorption capacity and vice versa. This implies that biochar samples with lower HI and OSI values may have higher adsorption capacities.

Carbonated carbon (CC) concentration varies among biochar types, with non-treated coffee husks having the highest, followed by treated coffee husks, treated coffee husks and banana peels, treated banana peels, non-treated banana peels, and non-treated banana peels/non-treated coffee husks. Total organic carbon (TOC) concentration follows a similar trend, with non-treated coffee husks having the highest concentration, followed by treated coffee husks, non-treated banana peels, treated coffee husks and banana peels, non-treated banana peels/non-treated coffee husks, and treated banana peels. These variations suggest that the source material and production process significantly influence biochar characteristics.

Bio-sorbents used for chromium removal have certain characteristics that are relevant to their effectiveness. These characteristics include the presence of functional groups responsible for biosorption of chromium (Garg et al., 2023). The biosorbents should have a large surface area and abundant availability of pores as active centers (Fadia et al., 2023). The biosorbents should also exhibit high adsorption capacities and strong binding sites (Bayuo, 2021). The pH of the wastewater plays a significant role in the adsorption efficiency of the biosorbents (Wang et al., 2019). The biosorbents should be able to reduce Cr(VI) to Cr(III) during the adsorption process (Aggarwal & Arora, 2020).

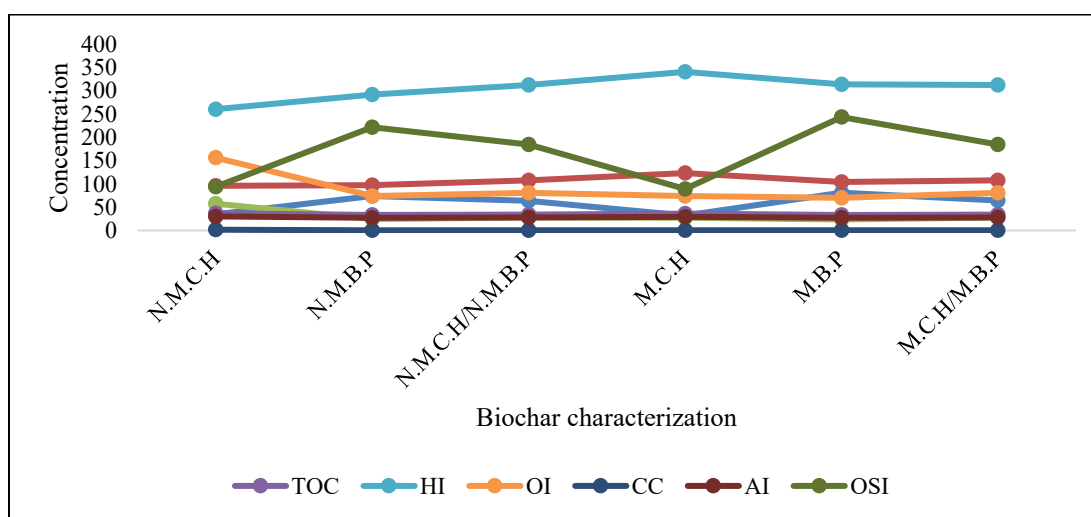


Figure 10: Biochar Characterization.

In the characterization of biochar presented in Figure 10, several parameters are analyzed across different types of biochar, providing insights into their properties and potential adsorption capacities.

The observed significantly high Hydrogen Index (HI) across all biochar samples, with the non-treated coffee husks and banana peels mixture showing the highest HI, suggests a potential inverse relationship with adsorption capacity (Bamdad et al., 2019). Higher HI values typically indicate lower adsorption capacity, implying that biochar samples with lower HI values may exhibit higher adsorption capacities (Ji et al., 2022).

Similarly, the inverse relationship between Hydrogen Index (HI) and Oil Saturation Index (OSI) with adsorption capacity highlights the importance of considering both parameters when assessing the potential adsorption capacities of biochar samples (Tian et al., 2024). Higher values of OSI and HI suggest lower adsorption capacity and vice versa.

The variations in carbonated carbon (CC) and total organic carbon (TOC) concentrations among different biochar types suggest that the source material and production process significantly influence biochar characteristics (Tian et al., 2024). Higher concentrations of CC and TOC may indicate a higher content of carbonaceous materials, which could potentially contribute to enhanced adsorption capacities (Hoang et al., 2023).

Previous studies like Saravanan & Kumar (2022) have emphasized the importance of carbonaceous materials in biochar for adsorption applications. According to Olugbenga et al. (2024) Carbonaceous materials provide active sites for the adsorption of contaminants such as chromium, contributing to the overall adsorption capacity of biochar.

Literature highlights several characteristics relevant to the effectiveness of bio-sorbents for chromium removal. These include the presence of functional groups responsible for bio-sorption, large surface area, abundant availability of pores as active centers, high adsorption capacities, strong binding sites, and the ability to reduce Cr (VI) to Cr (III) during the adsorption process (Javanbakht et al., 2013; Islam et al., 2023)

Biochar, with its porous structure and functional groups such as hydroxyl and carboxyl groups, has been recognized as an effective biosorbent for chromium removal (Jiang et al., 2023). The presence of these functional groups provides active sites for chromium adsorption, while the porous structure allows for a high surface area, facilitating efficient adsorption processes (Każmierczak et al., 2021).

4.4.2 Heavy metal effectiveness removal by the natural bio-absorbent

Figure 11, illustrates a case of chromium % removal by the bio-absorbent vs. Contact Time. It portrays that the removal percentage for Cr on the adsorbent consistently increases with prolonged contact time. The optimal removal of Cr occurs at a contact time of 60 minutes, with non-treated coffee husks achieving the highest removal efficiency of 98.83%, followed by treated coffee husks at 95.60% at the same contact time. Additionally, treated coffee husks and banana peels reaches 94.78% removal at 80 minutes, non-treated banana peels achieve 94.56% removal at 80 minutes, treated banana peels attains 90.23% removal at 80 minutes, and non-treated coffee husks and banana peels reaches 90.00% removal at 80 minutes. There was a positive correlation between contact time and removal efficiency for all biochar samples, indicating the influence of active binding sites and pores. Initially, there is an exponential increase in removal percentage for all adsorbents from 20 to 40 minutes, indicative of rapid engagement of active sites. Subsequently, there is a slight increase in removal percentage from 40 to 60 minutes, suggesting continued utilization of active sites. However, a linear slight decline is noted for non-treated coffee husks and treated coffee husks, while the rest of the biochar samples exhibit a slow increase from 60 to 80 minutes. The observed decline for non-treated coffee husks and treated coffee husks, and the slow increase for other biochar samples from 60 to 80 minute thus attainment of equilibrium. This equilibrium phase suggests a saturation of available binding sites and pores, leading to a stabilization in removal efficiency.

Biochar derived from coffee husks and banana peels has shown promising results in the removal of heavy metals through biosorption. Coffee husk biochar exhibited high sorption capacities for Pb^{2+} and Cd^{2+} ions, with maximum sorption capacities of 139.5 mg/g and 116.3 mg/g, respectively (Fu et al., 2022). Banana peel biochar also demonstrated efficient removal of heavy metals, specifically hexavalent chromium (Cr^{6+}) and copper (Cu^{2+}), from drinking water through

the adsorption process. The biosorption efficiency of banana peels increased with an increase in biosorbents dose and was influenced by factors such as pH, agitation speed, and initial metal concentration (Saleh & Ahmaed, 2023). The biochar derived from mixed waste, including banana peels and sludge, also showed effective adsorption of heavy metals such as Pb(II), Cu(II), and Zn(II), with a high adsorption rate for Cu(II) (Carnier et al., 2022). These findings highlight the potential of coffee husk and banana peel biochar as low-cost and efficient adsorbents for the removal of heavy metals from wastewater and drinking water.

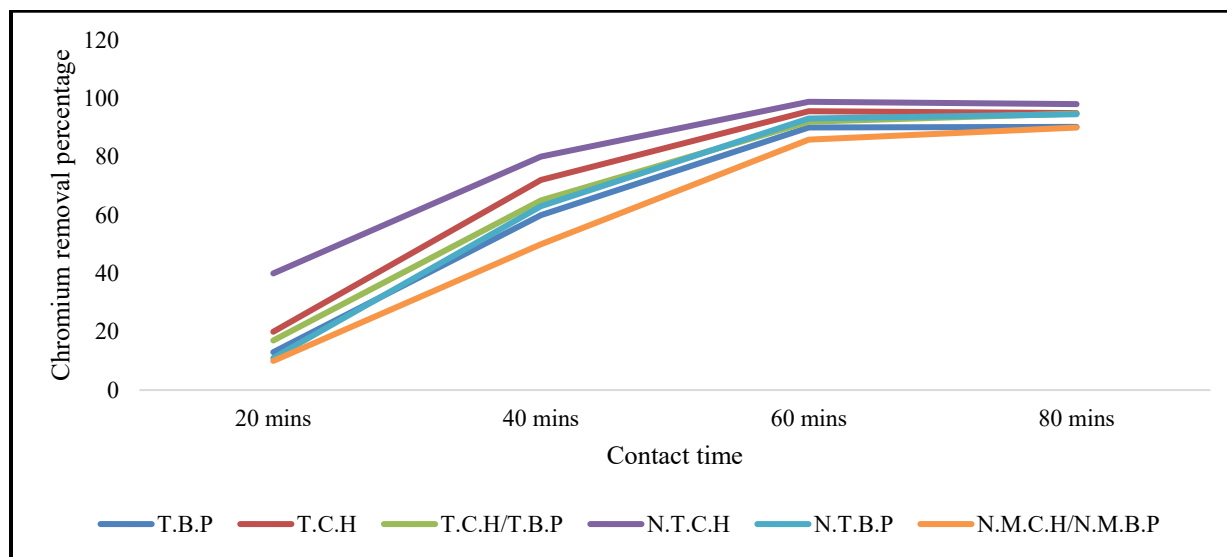


Figure 11: Chromium percentage removal vs contact time.

In Figure 11, the effectiveness of chromium removal by the natural bio-absorbent is depicted over varying contact times. The results indicate that the optimal removal of chromium occurs at a contact time of 60 minutes for all biochar samples. Among them, non-treated coffee husks exhibit the highest removal efficiency of 98.83%, followed closely by treated coffee husks at 95.60%. This suggests that both non-treated and treated coffee husks are highly effective in removing chromium from aqueous solutions within a relatively short contact time (Ayalew & Aragaw, 2020). The high removal efficiency of non-treated coffee husks could be attributed to their inherent properties, such as a high surface area, pore volume, and the presence of functional groups like hydroxyl and carboxyl groups, which facilitate chromium adsorption through surface complexation and ion exchange processes (Raji et al., 2023).

The positive correlation observed between contact time and removal efficiency indicates the importance of prolonged exposure for maximum chromium removal (Kumar et al., 2023). Initially, there is an exponential increase in removal percentage from 20 to 40 minutes, indicating rapid engagement of active binding sites and pores on the biochar surface (Kumkum & Kumar, 2024). Subsequently, from 40 to 60 minutes, there is a slight increase in removal percentage, suggesting continued utilization of active sites (Ali et al., 2016). This phase signifies the saturation of easily accessible binding sites, leading to a slower increase in removal efficiency (Al-Ghouti & Al-Absi, 2020). Beyond 60 minutes, a linear slight decline in removal percentage is observed for non-treated and treated coffee husks, while other biochar samples exhibit a slow increase in removal efficiency from 60 to 80 minutes. This phase indicates the attainment of equilibrium, where the rate of chromium adsorption becomes balanced with desorption, resulting in a stabilization of removal efficiency (Vunain et al., 2021).

The observed trend in chromium removal suggests the involvement of active binding sites and pores on the biochar surface. Initially, rapid adsorption occurs due to the availability of abundant active sites (Jiang et al., 2023). As the contact time increases, the adsorption process approaches equilibrium, with a gradual decline in removal efficiency for some biochar samples indicating saturation of available binding sites (Lee et al., 2019). This equilibrium phase highlights the balance between adsorption and desorption processes on the biochar surface (Wang, He, et al., 2023).

The variation in removal efficiencies among different biochar samples underscores the influence of biochar properties, such as surface area, pore structure, and functional groups, on chromium adsorption (Almutairi et al., 2023). Non-treated coffee husks demonstrate superior removal efficiency, possibly due to their inherent properties or specific surface chemistry favorable for chromium adsorption (Quyen et al., 2021). Treated coffee husks, treated coffee husks and banana peels, and non-treated banana peels also exhibit substantial chromium removal efficiencies, albeit slightly lower than non-treated coffee husks. These differences in removal efficiencies may be attributed to variations in biochar properties resulting from different production processes and feedstock materials (Wang, Wang, et al., 2024).

CHAPTER FIVE: CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

The following conclusions were drawn from the study;

- i. Tannery effluent heavy metal concentrations differ among studied sites with Cr and Pb concentration being higher and above national recommendable standards by NEMA at site 3 than at other sites. However, lower trace elements concentration in the wastewater at site 1 and site 2 may not mean no ongoing pollution activities but might be attributed to effectiveness of treatment methods of these effluents by the responsible industries before discharge.
- ii. Different biochar possess different characteristics, non-treated coffee husks has the best biosorbent properties in terms of total organic carbon, highest oxygen index, highest carbonated carbon, however, it also possessed the lowest hydrogen index and the lowest free oils. On the other hand, non-treated coffee husks combined with non-treated banana peel has the worst properties with least carbonated carbon, hydrogen index, and a relatively low oxygen index and total organic carbon
- iii. Non-treated coffee husks are the most effective natural bio-sorbents in removing heavy metal ions from discharged tannery effluents with removal efficiency of 98.83%, followed by treated coffee husks at 95.60% at the same contact time.

5.2 Recommendations

The following recommendations have been drawn from the study;

- i) Tannery leather industrialists should adopt the use of non-modified coffee husks as natural bio-sorbents in removing heavy metal ions from the tannery effluent before its discharge.
- ii) The treatment and synergy of the biochar is not recommended as it showed no added significance in comparison to un treated biochar of only coffee husks.
- iii) Hawk analysis should be adopted in the characterization of biomass materials especially those to be used in bioremediation.
- iv) Further research should be undertaken on the recycling and reuse of the adsorbed chromium and the biochar.

REFERENCES

- Abate, T. A., Desta, A. F., & Love, N. G. (2020). Evaluating tannery wastewater treatment performance based on physicochemical and microbiological characteristics: An Ethiopian case study. *Water Environment Research*, 93(5), 658–669. <https://doi.org/10.1002/wer.1364>
- Aggarwal, R., & Arora, G. (2020). Assessment of biosorbents for chromium removal from aqueous media. *Materials Today: Proceedings*, 28, 1540–1545. <https://doi.org/10.1016/j.matpr.2020.04.837>
- Akinnawo, S. (2023). Eutrophication: Causes, Consequences, Physical, Chemical and Biological Techniques for Mitigation Strategies. *Environmental Challenges*, 12, 100733–100733. <https://doi.org/10.1016/j.envc.2023.100733>
- Al-Ghouti, M. A., & Al-Absi, R. S. (2020). Mechanistic understanding of the adsorption and thermodynamic aspects of cationic methylene blue dye onto cellulosic olive stones biomass from wastewater. *Scientific Reports*, 10(1). <https://doi.org/10.1038/s41598-020-72996-3>
- Ali, A., Ibrahim, M., & Madhloom, H. (2016). Eggshell Powder As An Adsorbent for Removal of Cu (II) and Cd (II) from Aqueous Solution: Equilibrium, Kinetic and Thermodynamic Studies. *AlNahrain University, College of Engineering Journal*, 19, 186–193.
- Almutairi, A. A., Ahmad, M., Rafique, M. I., & Al-Wabel, M. I. (2023). Variations in composition and stability of biochars derived from different feedstock types at varying pyrolysis temperature. *Journal of the Saudi Society of Agricultural Sciences*, 22(1), 25–34. <https://doi.org/10.1016/j.jssas.2022.05.005>
- Ambaye, T. G., Vaccari, M., van Hullebusch, E. D., Amrane, A., & Rtimi, S. (2020). Mechanisms and adsorption capacities of biochar for the removal of organic and inorganic pollutants from industrial wastewater. *International Journal of Environmental Science and Technology*. <https://doi.org/10.1007/s13762-020-03060-w>
- Ankareddy, S., & Matli, C. S. (2023). Experimental Studies on the Removal of Chromium from Tannery Wastewater using Chemical Precipitation and Adsorption Techniques. *Current World Environment*, 18(1), 164–175. <https://doi.org/10.12944/cwe.18.1.15>
- Arti, & Mehra, R. (2023). Analysis of heavy metals and toxicity level in the tannery effluent and the environs. *Environmental Monitoring and Assessment*, 195(5). <https://doi.org/10.1007/s10661-023-11154-4>
- Asaduzzaman, M., Hasan, I., Rajia, S., Khan, N., & Kabir, K. A. (2014). Impact of tannery effluents on the aquatic environment of the Buriganga River in Dhaka, Bangladesh. *Toxicology and Industrial Health*, 32(6), 1106–1113. <https://doi.org/10.1177/0748233714548206>
- Ayalew, A. A., & Aragaw, T. A. (2020). Utilization of treated coffee husk as low-cost bio-sorbent for adsorption of methylene blue. *Adsorption Science & Technology*, 38(5-6), 205–222. <https://doi.org/10.1177/0263617420920516>

- Aziz, K., Mustafa, F., Omer, K. M., Hama, S., Hamarawf, R. F., & Kaiwan Othman Rahman. (2023). Heavy metal pollution in the aquatic environment: efficient and low-cost removal approaches to eliminate their toxicity: a review. *Heavy Metal Pollution in the Aquatic Environment: Efficient and Low-Cost Removal Approaches to Eliminate Their Toxicity: A Review*, 13(26), 17595–17610. <https://doi.org/10.1039/d3ra00723e>
- Baguma, G., Bamanya, G., Gonzaga, A., Ampaire, W., & Onen, P. (2023). A Systematic Review of Contaminants of Concern in Uganda: Occurrence, Sources, Potential Risks, and Removal Strategies. *Pollutants*, 3(4), 544–586. <https://doi.org/10.3390/pollutants3040037>
- Bakyayita, G., Norrström, A., & Kulabako, R. (2015). Competitive and noncompetitive batch sorption studies of aqueous Cd(II) and Pb(II) uptake onto *Coffea canephora* husks, *Cyperus papyrus* stems and *Musa* spp. peels. *Journal of Chemistry*, 2015, 17. doi:10.1155/2015/696098
- Bakyayita, G., Norrström, A., Nalubega, M., & Kulabako, R. (2014). Kinetic studies of Cd (II) and Pb (II) ions biosorption from aqueous media using untreated and chemically treated biosorbents. *Journal of Water Science and Technology*.
- Bamdad, H., Hawboldt, K., MacQuarrie, S., & Papari, S. (2019). Application of biochar for acid gas removal: experimental and statistical analysis using CO₂. *Environmental Science and Pollution Research*, 26(11), 10902–10915. <https://doi.org/10.1007/s11356-019-04509-3>
- Bamukyaye, S., & Wanasolo, W. (2017). Performance of Egg-shell and Fish scale as Adsorbent Materials for Chromium (VI) removal from Effluents of Tannery Industries in Eastern Uganda. *Open Access Library Journal*, 4(e3732). doi:10.4236/oalib.1103732
- Bao, Z.-Z., Chen, Z.-F., Lu, S.-Q., Wang, G., Qi, Z., & Cai, Z. (2021). Effects of hydroxyl group content on adsorption and desorption of anthracene and anthrol by polyvinyl chloride microplastics. *Science of the Total Environment*, 790, 148077–148077. <https://doi.org/10.1016/j.scitotenv.2021.148077>
- Basu, P. (2018). *Biomass Gasification, Pyrolysis and Torrefaction* | ScienceDirect. [Www.sciencedirect.com. https://www.sciencedirect.com/book/9780128129920/biomass-gasification-pyrolysis-and-torrefaction](https://www.sciencedirect.com/book/9780128129920/biomass-gasification-pyrolysis-and-torrefaction)
- Bayuo, J. (2021). An extensive review on chromium (vi) removal using natural and agricultural wastes materials as alternative biosorbents. *Journal of Environmental Health Science and Engineering*, 19(1), 1193–1207. <https://doi.org/10.1007/s40201-021-00641-w>
- Bhattacharya, S., & Chaudhari, D. S. (2014). Study on Structural, Mechanical and Functional Properties of Polyester Silica Nanocomposite Fabric. *International Journal of Pure and Applied Sciences and Technology*, 21, 43–52.
- Bibi, F., Hussain, R., Iqbal, N., Saeed, S., Waseem, M., Elkaeed, E. B., Al-Anazy, M. M., & Haq, S. (2023). Chemical Activation and Magnetization of Onion Waste Derived Carbon for

- Arsenic Removal. *Arabian Journal of Chemistry*, 16(10), 105118–105118. <https://doi.org/10.1016/j.arabjc.2023.105118>
- Bilal, M., & Kumar, A. (2023). Leather Industry - an overview | ScienceDirect Topics. *Sciencedirect.com*, 9. <https://www.sciencedirect.com/topics/earth-and-planetary-sciences/leather-industry>
- Bilotta, G. S., & Brazier, R. E. (2008). Understanding the influence of suspended solids on water quality and aquatic biota. *Water Research*, 42(12), 2849–2861. <https://doi.org/10.1016/j.watres.2008.03.018>
- Bio-met. (Retrieved 10 23, 2018). *Bio-met Bioavailabilit Tool*. Retrieved from <http://www.bio-met.net>
- Bishnoi, N., Kumar, R., Kumar, S., & Rani, S. (2007). Biosorption of Cd(II) from aqueous solution using algal biomass spirogyra spp. *Journal of Hazardous Materials*, 145, 142–147.
- Bhuvanesh Kumar Sharma, & Singh, P. (2020). An Overview on Toxicity, Detection, and Removal of Chromium in Water and WasteWater. *Springer Transactions in Civil and Environmental Engineering*, 15–23. https://doi.org/10.1007/978-981-32-9956-6_2
- Boateng, T. K., Opoku, F., Acquah, S. O., & Akoto, O. (2015). Pollution evaluation, sources and risk assessment of heavy metals in hand-dug wells from Ejisu-Juaben Municipality, Ghana. *Environmental systems research*, 4(1), 1–12.
- Bwapwa, J. K., Nonsindiso Mkhize, & Seyam, M. (2024). EVALUATION OF OPERATIONAL EFFICIENCY AND PERFORMANCE FOR A WATER TREATMENT PLANT. *South African Journal of Chemical Engineering*, 49, 11–34. <https://doi.org/10.1016/j.sajce.2024.04.003>
- Carnier, R., Coscione, A. R., Abreu, C. A. de, Melo, L. C. A., & Silva, A. F. da. (2022). Cadmium and lead adsorption and desorption by coffee waste-derived biochars. *Bragantia*, 81. <https://doi.org/10.1590/1678-4499.20210142>
- Caroline Borges Agustini, Taysnara Simioni, Pinheiro, N., Hansen, É., Kopp, V., & Mariliz Gutterres. (2022). Recovery and Disposal of Tannery Waste Containing Toxic Metals. *CRC Press EBooks*, 94–116. <https://doi.org/10.1201/9781003138907-6>
- Chaudhary, P., Chhokar, V., Kumar, A., & Beniwal, V. (2017). Bioremediation of Tannery Wastewater. *Advances in Environmental Biotechnology*, 125 - 144. doi:10.1007/978-981-10-4041-2_7
- Chen, R.-Q., Zhao, X., Jiao, J., Li, Y., & Wei, M. (2019). *Surface-Modified Biochar with Polydentate Binding Sites for the Removal of Cadmium*. 20(7), 1775–1775. <https://doi.org/10.3390/ijms20071775>

- Dessinioti, C., & Stratigos, A. J. (2022). An Epidemiological Update on Indoor Tanning and the Risk of Skin Cancers. *Current Oncology*, 29(11), 8886–8903. <https://doi.org/10.3390/currncol29110699>
- Devi, D., Srinivasan, G., S. Kothandaraman, & S. Ashok Kumar. (2020). State-of-the-Art Review—Methods of Chromium Removal from Water and Wastewater. *Springer EBooks*, 37–51. https://doi.org/10.1007/978-981-15-5101-7_4
- Dharmaraj, R S. Gopikumar, P Ebby Darnay, S. Uma, Sundararajan, S., U. Muthuraman, & S Maruvarasan. (2021). Appraisal of Green Construction Material by Optimizing the Strength of Tannery Sludge Concrete. *IOP Conference Series*, 1145(1), 012003–012003. <https://doi.org/10.1088/1757-899x/1145/1/012003>
- Díaz, B., Sommer-Márquez, A., Ordoñez, P. E., Bastardo-González, E., Ricaurte, M., & Navas-Cárdenas, C. (2024). Synthesis Methods, Properties, and Modifications of Biochar-Based Materials for Wastewater Treatment: A Review. *Resources (Basel)*, 13(1), 8–8. <https://doi.org/10.3390/resources13010008>
- Dong, X., Chu, Y., Tong, Z., Sun, M., Meng, D., Yi, X., Gao, T., Wang, M., & Duan, J. (2024). Mechanisms of adsorption and functionalization of biochar for pesticides: A review. *Ecotoxicology and Environmental Safety*, 272, 116019. <https://doi.org/10.1016/j.ecoenv.2024.116019>
- Fadia Khadoudja Bensenane Dhina, Nouredine Nassrallah, & Abderrahim Choukchou-Braham. (2023). Comparison of Two Different Biosorbents for Heavy Metal Removal. *Chemical Engineering & Technology*, 46(4), 654–662. <https://doi.org/10.1002/ceat.202200130>
- Fatima, Q., Azhar Ali Haidry, Yao, Z., He, Y., Li, Z., Sun, L., & Xie, L. (2019). The critical role of hydroxyl groups in water vapor sensing of graphene oxide. *Nanoscale Advances*, 1(4), 1319–1330. <https://doi.org/10.1039/c8na00135a>
- Feng, L., Liu, X., Song, L., Wang, X., Zhang, Y., Cui, T., & Tang, H. (2013). The effect of alkali treatment on some physico–chemical properties of Xilinhaote lignite. *Powder Technology*, 247, 19–23. <https://doi.org/10.1016/j.powtec.2013.06.037>
- Fu, H., Wei, C., Qu, X., Li, H., & Zhu, D. (2018). *Strong binding of apolar hydrophobic organic contaminants by dissolved black carbon released from biochar: A mechanism of pseudomicelle partition and environmental implications*. 232, 402–410. <https://doi.org/10.1016/j.envpol.2017.09.053>
- Fu, L., Li, J., Wang, G., Luan, Y., & Dai, W. (2021). Adsorption behavior of organic pollutants on microplastics. *Ecotoxicology and Environmental Safety*, 217, 112207. <https://doi.org/10.1016/j.ecoenv.2021.112207>
- Fu, Y., Hua, S., Yang, Y., Yang, S., Zhang, Y., & Zhang, G. (2022). Characterization, efficiency and mechanism in removing heavy metals by a mixed biochar derived from sludge and banana peel. *DESALINATION and WATER TREATMENT*, 249, 232–245. <https://doi.org/10.5004/dwt.2022.28134>

- Garg, R., Garg, R., Sillanpää, M., Alimuddin, Khan, M. A., Mubarak, N. M., & Tan, Y. H. (2023). Rapid adsorptive removal of chromium from wastewater using walnut-derived biosorbents. *Scientific Reports*, 13(1), 6859. <https://doi.org/10.1038/s41598-023-33843-3>
- Garg, S., Tripathi, M., & Srinathi, T. (2012). Strategies for Chromium Bioremediation. In *Reviews of Environmental Contamination and Toxicology* (Vol. 217, pp. 70-140). Bangalore: Springer Science+Business Media, LLC. doi:10.1007/978-1-4614-2329-4_2
- Ghalib, H. B. (2017). Groundwater chemistry evaluation for drinking and irrigation utilities in east Wasit province, Central Iraq. *Applied Water Science*, 7(7), 3447–3467. <https://doi.org/10.1007/s13201-017-0575-8>
- Gryta, A., Skic, K., Adamczuk, A., Skic, A., Marciniak, M., Grzegorz Józefaciuk, & Patrycja Boguta. (2023). The Importance of the Targeted Design of Biochar Physicochemical Properties in Microbial Inoculation for Improved Agricultural Productivity—A Review. *Agriculture*, 14(1), 37–37. <https://doi.org/10.3390/agriculture14010037>
- Gustafsson, J. (2012). *Visual MINTEQ, ver 3.0*. Stockholm, Sweden: Department of Land and Water Resources Engineering, Royal Institute of Technology - KTH. Retrieved from [http://www.lwr.kth.se/English/Our Software/vminteq/](http://www.lwr.kth.se/English/Our%20Software/vminteq/)
- Gopolang, O. P., & Letshwenyo, M. W. (2019). Water Quality Index of Waste Stabilisation Ponds and Downstream of Discharge Point. *Journal of Environmental Protection*, 10(08), 993–1005. <https://doi.org/10.4236/jep.2019.108059>
- Haider, F. U., Wang, X., Zulfikar, U., Farooq, M., Hussain, S., Mehmood, T., Naveed, M., Li, Y., Liquin, C., Saeed, Q., Ahmad, I., & Mustafa, A. (2022). Biochar application for remediation of organic toxic pollutants in contaminated soils; An update. *Ecotoxicology and Environmental Safety*, 248, 114322. <https://doi.org/10.1016/j.ecoenv.2022.114322>
- Haroun, M., Idris, A., & Omer, S. (2007). A study of heavy metals and their fate in the composting of tannery sludge. *Waste Management*, 1541 - 1550.
- Hasegawa, M., Barbosa, A., & Takashima, K. (2011). Biotreatment of industrial tannery wastewater using *Botryosphaeria rhodina*. *Journal Serbian Chemical Society*, 76, 1 - 8.
- Hashem, Md. A., Payel, S., Mim, S., Hasan, Md. A., Nur-A-Tomal, Md. S., Rahman, Md. A., & Sarker, M. I. (2022). Chromium adsorption on surface activated biochar made from tannery liming sludge: A waste-to-wealth approach. *Water Science and Engineering*, 15(4), 328–336. <https://doi.org/10.1016/j.wse.2022.09.001>
- He, H., Zhang, R., Zhang, P., Wang, P., Chen, N., Qian, B., Zhang, L., Yu, J., & Dai, B. (2023). Functional Carbon from Nature: Biomass-Derived Carbon Materials and the Recent Progress of Their Applications. *Advanced Science*, 10(16). <https://doi.org/10.1002/advs.202205557>

- He, Z., Wang, C., Cao, H., Liang, J., Pei, S., & Li, Z. (2023). Nitrate Absorption and Desorption by Biochar. *Agronomy*, 13(9), 2440. <https://doi.org/10.3390/agronomy13092440>
- Hoang, T.-D., Bandh, S. A., Malla, F. A., Irteza Qayoom, Bashir, S., Suhail Bashir Peer, & Halog, A. (2023). Carbon-Based Synthesized Materials for CO₂ Adsorption and Conversion: Its Potential for Carbon Recycling. *Recycling*, 8(4), 53–53. <https://doi.org/10.3390/recycling8040053>
- Islam, Md. M., Mohana, A. A., Rahman, Md. A., Rahman, M., Naidu, R., & Rahman, M. M. (2023). A Comprehensive Review of the Current Progress of Chromium Removal Methods from Aqueous Solution. *Toxics*, 11(3), 252. <https://doi.org/10.3390/toxics11030252>
- Jagadeesh, N., & Sundaram, B. (2023). Adsorption of Pollutants from Wastewater by Biochar: A Review. *Journal of Hazardous Materials Advances*, 9, 100226. <https://doi.org/10.1016/j.hazadv.2022.100226>
- Janu, R., Mrlik, V., Ribitsch, D., Hofman, J., Sedláček, P., Bielská, L., & Soja, G. (2021). Biochar surface functional groups as affected by biomass feedstock, biochar composition and pyrolysis temperature. *Carbon Resources Conversion*, 4, 36–46. <https://doi.org/10.1016/j.crcon.2021.01.003>
- Javanbakht, V., Alavi, S. A., & Zilouei, H. (2013). Mechanisms of heavy metal removal using microorganisms as biosorbent. *Water Science and Technology*, 69(9), 1775–1787. <https://doi.org/10.2166/wst.2013.718>
- Ji, Y., Zhang, C., Zhang, X. J., Xie, P. F., Wu, C., & Jiang, L. (2022). A high adsorption capacity bamboo biochar for CO₂ capture for low temperature heat utilization. *Separation and Purification Technology*, 293, 121131. <https://doi.org/10.1016/j.seppur.2022.121131>
- Jiang, X., Liu, Y., Yin, X., Deng, Z., Zhang, S., Ma, C., & Wang, L. (2023). Efficient removal of chromium by a novel biochar-microalga complex: Mechanism and performance. *Environmental Technology & Innovation*, 31, 103156–103156. <https://doi.org/10.1016/j.eti.2023.103156>
- Kapoor, R. T., & Zdarta, J. (2024). Fabrication of Engineered Biochar for Remediation of Toxic Contaminants in Soil Matrices and Soil Valorization. *Chemosphere*, 142101–142101. <https://doi.org/10.1016/j.chemosphere.2024.142101>
- Kaźmierczak, B., Molenda, J., & Swat, M. (2021). The adsorption of chromium (III) ions from water solutions on biocarbons obtained from plant waste. *Environmental Technology & Innovation*, 23, 101737–101737. <https://doi.org/10.1016/j.eti.2021.101737>
- Kiggundu, N., & Sittamukyoto, J. (2019). Pyrolysis of Coffee Husks for Biochar Production. *Journal of Environmental Protection*, 10(12), 1553–1564. <https://doi.org/10.4236/jep.2019.1012092>
- Kumar, M., N.S. Maurya, Singh, A., & Rai, M. K. (2023). Efficient removal of Cr (VI) from aqueous solution by using tannery by-product (Buffing Dust). *Heliyon*, 9(4), e15038–e15038. <https://doi.org/10.1016/j.heliyon.2023.e15038>
- Kumar P.S, & G. Janet Joshiba. (2020). *Environmental and Chemical Issues in Tanneries and Their Mitigation Measures*. https://doi.org/10.1007/978-981-15-6296-9_1

- Kumkum, P., & Kumar, S. (2024). A Review on Biochar as an Adsorbent for Pb(II) Removal from Water. *Biomass*, 4(2), 243–272. <https://doi.org/10.3390/biomass4020012>
- Kwon, G., Cho, D.-W., Jang, H., Shiung Lam, S., & Song, H. (2022). Synergistic effects of blending seafood wastes as Co-pyrolysis feedstock on syngas production and biochar properties. *Chemical Engineering Journal*, 429, 132487. <https://doi.org/10.1016/j.cej.2021.132487>
- Lapworth, D., Nkhuwa, D., Okotto-Okotto, J., Pedley, S., Stuart, M., Tijani, M., & Wright, J. (2017). Urban groundwater quality in sub-Saharan Africa: current status and implications for water security and public health. *Hydrogeology Journal*, 25(4), 1093–1116.
- Lee, S. Y., Choi, J.-W., Song, K. G., Choi, K., Lee, Y. J., & Jung, K.-W. (2019). Adsorption and mechanistic study for phosphate removal by rice husk-derived biochar functionalized with Mg/Al-calcined layered double hydroxides via co-pyrolysis. *Composites Part B: Engineering*, 176, 107209. <https://doi.org/10.1016/j.compositesb.2019.1072>
- Luo, M., Jiang, X., Liu, Y., Liu, Y., Yu, H., Niu, Y., Meng, X., Wang, L., & Niu, Y. (2023). Enhanced adsorption complexation of biochar by nitrogen-containing functional groups. *Journal of Environmental Chemical Engineering*, 11(6), 111194–111194. <https://doi.org/10.1016/j.jece.2023.111194>
- Magona, N. (2022). Constraints towards the development of leather , hides and skins industry in uganda. *Www.academia.edu*. Retrieved December 9, 2023, from https://www.academia.edu/12695888/Constraints_towards_the_development_of_leather_hides_and_skins_industry_in_uganda
- Martin, J. M., Ghaferi, J. M., Cummins, D. L., Mamelak, A. J., Schmults, C. D., Parikh, M., Speyer, L.-A., Chuang, A., Richardson, H. V., Stein, D., & Liégeois, N. J. (2009). CHANGES in SKIN TANNING ATTITUDES Fashion Articles and Advertisements in the Early 20th Century. *American Journal of Public Health*, 99(12), 2140–2146. <https://doi.org/10.2105/AJPH.2008.144352>
- Mathes, S., Lindwedel, K. S., Nilsen, L. T., Kaiser, I., Pfahlberg, A. B., & Gefeller, O. (2023). Global Tanning Bed Advertising: A Comparison of Legal Regulations on Three Continents. *Cancers*, 15(17), 4362. <https://doi.org/10.3390/cancers15174362>
- Minas, F., Chandravanshi, B., & Leta, S. (2017). Chemical precipitation method for chromium removal and its recovery from tannery wastewater in Ethiopia. *Chemistry International*, 3, 291–305.
- Mohammed, K. (2017). *Tannery Waste Management: Challenges and Opportunities*.
- Morera, J. M., Borri, E., Zsembinszki, G., Vérez, D., Gasa, G., Bartolí, E., & Cabeza, L. F. (2023). Energy Assessment of a Tannery to Improve Its Sustainability. *Sustainability*, 15(6), 5599–5599. <https://doi.org/10.3390/su15065599>
- Murtaza, G., Ahmed, Z., Valipour, M., Ali, I., Usman, M., Iqbal, R., Usman Zulfikar, Rizwan, M., Mahmood, S., Ullah, A., Arslan, M., Muhammad, Ditta, A., & Tariq, A. (2024). Recent trends and economic significance of modified/functionalized biochars for remediation of

- environmental pollutants. *Scientific Reports*, 14(1). <https://doi.org/10.1038/s41598-023-50623-1>
- Mwinyihija, M. (2010). Ecotoxicological diagnosis in the tanning industry. *Springer Science Business Media, LLC*, 17. doi:10.1007/978-1-4419-6266-9-2
- Mwinyihija, M., Meharg, A., Dawson, J., Strachan, N. J. C., & 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. <https://doi.org/10.1007/s00244-005-1049-9>
- NAPE. (2009). *The Leather -Tannery Industry in Uganda*. Kampala.
- Ndung, W. (2019). Evaluating the surface functional groups on banana leaf petioles and the resultant biochar for potential adsorbance. *J. Mater. Environ. Sci*, 10(2), 255–261. https://www.jmaterenvironsci.com/Document/vol11/vol11_N2/JMES-2020-11-23-Ndungu.pdf
- Nyenje, P., Foppen, J., Uhlenbrook, S., & Lutterodt, G. (2014). Using hydrochemical tracers to assess impacts of unsewered urban catchments on hydrochemistry and nutrients in groundwater. *Hydrological Processes*, 28(24), 5860-5878.
- Nur-E-Alam, Md., Mia, Md. A. S., Ahmad, F., & Rahman, Md. M. (2020). An overview of chromium removal techniques from tannery effluent. *Applied Water Science*, 10(9). <https://doi.org/10.1007/s13201-020-01286-0>
- Oliveira, W. E., Franca, A. S., Oliveira, L. S., & Rocha, S. D. (2008). Untreated coffee husks as biosorbents for the removal of heavy metals from aqueous solutions. *Journal of Hazardous Materials*, 152(3), 1073–1081. <https://doi.org/10.1016/j.jhazmat.2007.07.085>
- Pantaleo, P., Komakech, H. C., Mtei, K. M., & Njau, K. N. (2018). Contamination of groundwater sources in emerging African towns: The case of Babati town, Tanzania. *Water Practice & Technology*, 13(4), 980-990.
- Patel, N., Shahane, S., Chauhan, D., Rai, D., Khan, Md. Z. A., Bhunia, B., & Chaudhary, V. K. (2021). Environmental Impact and Treatment of Tannery Waste. *Environmental Chemistry for a Sustainable World*, 577–595. https://doi.org/10.1007/978-3-030-52395-4_16
- Perkumienė, D., Atalay, A., Safaa, L., & Grigienė, J. (2023). Sustainable Waste Management for Clean and Safe Environments in the Recreation and Tourism Sector: A Case Study of Lithuania, Turkey and Morocco. *Recycling*, 8(4), 56. <https://doi.org/10.3390/recycling8040056>

- Qasem, N. A. A., Mohammed, R. H., & Lawal, D. U. (2021). Removal of heavy metal ions from wastewater: a comprehensive and critical review. *Npj Clean Water*, 4(1), 1–15. <https://doi.org/10.1038/s41545-021-00127-0>
- Quyen, V. thi, Pham, T. - H., Kim, J., Thanh, D. M., Thang, P. Q., Van Le, Q., Jung, S. H., & Kim, T. (2021). Biosorbent derived from coffee husk for efficient removal of toxic heavy metals from wastewater. *Chemosphere*, 284, 131312. <https://doi.org/10.1016/j.chemosphere.2021.131312>
- Raji, Z., Karim, A., Karam, A., & Seddik Khalloufi. (2023). Adsorption of Heavy Metals: Mechanisms, Kinetics, and Applications of Various Adsorbents in Wastewater Remediation—A Review. *Waste*, 1(3), 775–805. <https://doi.org/10.3390/waste1030046>
- Rangabhashiyam, S., & Balasubramanian, P. (2019). The potential of lignocellulosic biomass precursors for biochar production: Performance, mechanism and wastewater application—A review. *Industrial Crops and Products*, 128, 405–423. <https://doi.org/10.1016/j.indcrop.2018.11.041>
- Rigueto, C. V. T., Rosseto, M., Krein, D. D. C., Ostwald, B. E. P., Massuda, L. A., Zanella, B. B., & Dettmer, A. (2020). Alternative uses for tannery wastes: a review of environmental, sustainability, and science. *Journal of Leather Science and Engineering*, 2(1). <https://doi.org/10.1186/s42825-020-00034-z>
- Ruffins, R. (2015). The Industrial Impact on Wetlands in Jinja and the Nexus of Industry, Wetlands, and Community (A Rights-Based Sustainable Development Approach).
- Saleh, S., & Asmaa Sabah Ahmaed. (2023). EFFICIENCY OF SOME CHEAP MATERIALS IN REMOVING SOME HEAVY METALS. *MINAR International Journal of Applied Sciences and Technology*, 05(01), 130–139. <https://doi.org/10.47832/2717-8234.14.13>
- Samrithi, A., & Usha, K. (2012). Isolation and characterization of chromium removing bacteria from tannery effluent disposal site. *International Journal Advanced Biotechnology Research*, 3(3), 644 - 652.
- Samuel Olugbenga, O., Goodness Adeleye, P., Blessing Oladipupo, S., Timothy Adeleye, A., & Igenepo John, K. (2024). Biomass-derived biochar in wastewater treatment- a circular economy approach. *Waste Management Bulletin*, 1(4), 1–14. <https://doi.org/10.1016/j.wmb.2023.07.007>
- Saravanan, A., & Kumar, P. S. (2022). Biochar derived carbonaceous material for various environmental applications: Systematic review. *Environmental Research*, 214, 113857. <https://doi.org/10.1016/j.envres.2022.113857>
- Sasivarman, B., Rajeshkannan, M., Sowmiya, V., Subashchandrabose, E., & Swetha, R. (2018). Evaluation of Anaerobic Digester for Treating Tannery Effluent by Water Displacement Method. *International Journal of Engineering & Technology*, 7(4.2), 40. <https://doi.org/10.14419/ijet.v7i4.2.26328>

- Sawalha, H., Al-Jabari, M., Elhamouz, A., Abusafa, A., & Rene, E. R. (2020). Tannery wastewater treatment and resource recovery options. *Waste Biorefinery*, 679–705. <https://doi.org/10.1016/b978-0-12-818228-4.00025-3>
- Scaria, J., Gopinath, A., Ranjith, N., Ravindran, V., Safar Ummar, Puthiya Veetil Nidheesh, & Kumar, M. (2022). Carbonaceous materials as effective adsorbents and catalysts for the removal of emerging contaminants from water. *Journal of Cleaner Production*, 350, 131319–131319. <https://doi.org/10.1016/j.jclepro.2022.131319>
- Shahib, I. I., Iftikhar, J., Oyekunle, D. T., Elkhilfi, Z., Jawad, A., Wang, J., Lei, W., & Chen, Z. (2022). Influences of chemical treatment on sludge derived biochar; Physicochemical properties and potential sorption mechanisms of lead (II) and methylene blue. *Journal of Environmental Chemical Engineering*, 10(3), 107725. <https://doi.org/10.1016/j.jece.2022.107725>
- Singh, P., Kumar, V., Rathaur, P., Singh, R., & Singh, P. (2023). *Toxic Impact of Tannery Waste Water on Human Health, Plants and Aquatic EcosystemA review*. 10, 245.
- Srivatsav, P., Bhargav, B. S., Shanmugasundaram, V., Arun, J., Gopinath, K. P., & Bhatnagar, A. (2020). Biochar as an Eco-Friendly and Economical Adsorbent for the Removal of Colorants (Dyes) from Aqueous Environment: A Review. *Water*, 12(12), 3561. <https://doi.org/10.3390/w12123561>
- Ssemanda, & Kassim. (2018). *Wastewater treatment practices by tanneries: Case of Skyfat Tannery and Leather Industries of Uganda Tanneries, Jinja, Uganda*. Makerere University, Environmental Studies, Kampala.
- Subramani, T., & Haribalaji, D. (2012). Biodegradation of tannery effluent and designing the reactor for clarifier and activated sludge process. *Int J Mod Eng Res*, 2(3), 774 - 781
- Sukhenko, S. (1995). Relation between mercury concentration and water discharge in the Katun River, Siberia. *Marine and Freshwater Research*, 46(1), 245. <https://doi.org/10.1071/mf9950245>
- Suresh, K., Tang, T., T.H, M., Marc F.P. Bierkens, Maryna Strokai, Florian Sorger-Domenigg, & Wada, Y. (2023). Recent advancement in water quality indicators for eutrophication in global freshwater lakes. *King Abdullah University of Science and Technology Repository (King Abdullah University of Science and Technology)*. <https://doi.org/10.5194/egusphere-egu23-7565>
- Tadesse, G. L. (2017). Impacts of Tannery Effluent on Environments and Human Health: A Review Article. *Advances in Life Science and Technology*, 54, 58–67. <https://typeset.io/papers/impacts-of-tannery-effluent-on-environments-and-human-health-4ns3eb5qcx>
- Tadesse, G. L., & Guya, T. K. (2017). Impact of tannery effluent on environments and human health - A Review Article. *Advances in Life Sciences and Technology*, 54. <https://core.ac.uk/download/pdf/234687486.pdf>
- Taherymoosavi, S., Verheyen, V., Munroe, P., Joseph, S., & Reynolds, A. (2017). Characterization of organic compounds in biochars derived from municipal solid waste. *Waste Management*, 67, 131–142. <https://doi.org/10.1016/j.wasman.2017.05.052>

- Temsch, R., & Marchich, M. (2002). *Evaluation Report UNIDO Projects, US/UGA/92/200*. <https://www.oecd.org/countries/uganda/35480777.pdf>
- Tomczyk, A., Kondracki, B., & Katarzyna Szewczuk-Karpisz. (2022). *Chemical modification of biochars as a method to improve its surface properties and efficiency in removing xenobiotics from aqueous media*. 312, 137238–137238. <https://doi.org/10.1016/j.chemosphere.2022.137238>
- Tomczyk, A., Sokołowska, Z., & Boguta, P. (2020). Biochar physicochemical properties: pyrolysis temperature and feedstock kind effects. *Reviews in Environmental Science and Bio/Technology*, 19(1), 191–215. <https://doi.org/10.1007/s11157-020-09523-3>
- Torrise, A., Mellot-Draznieks, C., & Bell, R. G. (2010). Impact of ligands on CO₂ adsorption in metal-organic frameworks: First principles study of the interaction of CO₂ with functionalized benzenes. II. Effect of polar and acidic substituents. *The Journal of Chemical Physics*, 132(4), 044705. <https://doi.org/10.1063/1.3276105>
- Trazzi, P. A., Vashishtha, M., Najser, J., Schmalenberger, A., Kannuchamy, V. K., Leahy, J. J., & Kwapinski, W. (2024). Adsorption of Ammonium, Nitrate, and Phosphate on Hydrochars and Biochars. *Applied Sciences*, 14(6), 2280. <https://doi.org/10.3390/app14062280>
- Tumolo, M., Ancona, V., De Paola, D., Losacco, D., Campanale, C., Massarelli, C., & Uricchio, V. F. (2020). Chromium Pollution in European Water, Sources, Health Risk, and Remediation Strategies: An Overview. *International Journal of Environmental Research and Public Health*, 17(15), 5438. <https://doi.org/10.3390/ijerph17155438>
- Vigiak, O., Grizzetti, B., Udias-Moinelo, A., Zanni, M., Dorati, C., Bouraoui, F., & Pistocchi, A. (2019). Predicting biochemical oxygen demand in European freshwater bodies. *Science of the Total Environment*, 666, 1089–1105. <https://doi.org/10.1016/j.scitotenv.2019.02.252>
- Vunain, E., Njewa, J. B., Biswick, T. T., & Ipadeola, A. K. (2021). Adsorption of chromium ions from tannery effluents onto activated carbon prepared from rice husk and potato peel by H₃PO₄ activation. *Applied Water Science*, 11(9). <https://doi.org/10.1007/s13201-021-01477-3>
- Vuong, T. X., Stephen, J., Thu, T., Cao, V., & Thuy, D. (2023). Insight into the Speciation of Heavy Metals in the Contaminated Soil Incubated with Corn Cob-Derived Biochar and Apatite. *Molecules*, 28(5), 2225–2225. <https://doi.org/10.3390/molecules28052225>
- Wang, B., Sun, Y.-C., & Sun, R.-C. (2019). Fractional and structural characterization of lignin and its modification as biosorbents for efficient removal of chromium from wastewater: a review. *Journal of Leather Science and Engineering*, 1(1). <https://doi.org/10.1186/s42825-019-0003-y>
- Wang, S., Ai, S., Nzediegwu, C., Kwak, J.-H., Islam, S., Li, Y., & Chang, S. X. (2020). Carboxyl and hydroxyl groups enhance ammonium adsorption capacity of iron (III) chloride and hydrochloric acid modified biochars. *Bioresource Technology*, 309, 123390–123390. <https://doi.org/10.1016/j.biortech.2020.123390>

- Wang, Y., Chen, L., Zhu, Y., Fang, W., Tan, Y., He, Z., & Liao, H. (2024). Research status, trends, and mechanisms of biochar adsorption for wastewater treatment: a scientometric review. *Environmental Sciences Europe*, 36(1). <https://doi.org/10.1186/s12302-024-00859-z>
- Wang, Y., Wang, K., Wang, X., Zhao, Q., Jiang, J., & Jiang, M. (2024). Effect of different production methods on physicochemical properties and adsorption capacities of biochar from sewage sludge and kitchen waste: Mechanism and correlation analysis. *Journal of Hazardous Materials*, 461, 132690–132690. <https://doi.org/10.1016/j.jhazmat.2023.132690>
- Wu, X., Quan, W., Chen, Q., Gong, W., & Wang, A. (2024). Efficient Adsorption of Nitrogen and Phosphorus in Wastewater by Biochar. *Molecules*, 29(5), 1005. <https://doi.org/10.3390/molecules29051005>
- Xing, J., Xu, G., & Li, G. (2021). Comparison of pyrolysis process, various fractions and potential soil applications between sewage sludge-based biochars and lignocellulose-based biochars. *Ecotoxicology and Environmental Safety*, 208, 111756. <https://doi.org/10.1016/j.ecoenv.2020.111756>
- Yaashikaa, P. P., & Kumar, P. S. (2020). A critical review on the biochar production techniques, characterization, stability and applications for circular bioeconomy. *Biotechnology Reports*, 28, e00570. <https://doi.org/10.1016/j.btre.2020.e00570>
- Yang, K., Yang, J., Jiang, Y., Wu, W., & Lin, D. (2016). Correlations and adsorption mechanisms of aromatic compounds on a high heat temperature treated bamboo biochar. *Environmental Pollution*, 210, 57–64. <https://doi.org/10.1016/j.envpol.2015.12.004>
- Yang, Y., Piao, Y., Wang, R., Su, Y., Liu, N., & Lei, Y. (2022). Nonmetal function groups of biochar for pollutants removal: A review. *Journal of Hazardous Materials Advances*, 8, 100171–100171. <https://doi.org/10.1016/j.hazadv.2022.100171>
- Yang, Y., Piao, Y., Wang, R., Su, Y., Qiu, J., & Liu, N. (2022). Mechanism of biochar functional groups in the catalytic reduction of tetrachloroethylene by sulfides. *Environmental Pollution*, 300, 118921–118921. <https://doi.org/10.1016/j.envpol.2022.118921>
- Yao, B., & Zhou, Y. (2022). Biochars' potential role in the remediation, revegetation, and restoration of contaminated soils. *Elsevier EBooks*, 381–399. <https://doi.org/10.1016/b978-0-323-85343-9.00013-6>
- Younas, F., Bibi, I., Afzal, M., Al-Misned, F., Niazi, N. K., Hussain, K., Shahid, M., Shakil, Q., Ali, F., & Wang, H. (2023). Unveiling Distribution, Hydrogeochemical Behavior and Environmental Risk of Chromium in Tannery Wastewater. *Water*, 15(3), 391. <https://doi.org/10.3390/w15030391>
- Yu, Q., Feng, J., Li, J., He, A., & G. Daniel Sheng. (2021). Mechanisms of aromatic molecule - Oxygen-containing functional group interactions on carbonaceous material surfaces. *Chemosphere*, 275, 130021–130021. <https://doi.org/10.1016/j.chemosphere.2021.130021>
- Zebron Phiri, Moja, N. T., Thabo T.I. Nkambule, & Lueta-Ann de Kock. (2024). Utilization of biochar for remediation of heavy metals in aqueous environments: A review and

- bibliometric analysis. *Heliyon*, 10(4), e25785–e25785. <https://doi.org/10.1016/j.heliyon.2024.e25785>
- Zhou, Q., Yang, N., Li, Y., Ren, B., Ding, X., Bian, H., & Yao, X. (2020). Total concentrations and sources of heavy metal pollution in global river and lake water bodies from 1972 to 2017. *Global Ecology and Conservation*, 22, e00925. <https://doi.org/10.1016/j.gecco.2020.e00925>
- Zhou, X.-Y., & Wang, X.-R. (2019). Impact of industrial activities on heavy metal contamination in soils in three major urban agglomerations of China. *Journal of Cleaner Production*, 230, 1–10. <https://doi.org/10.1016/j.jclepro.2019.05.098>
- Zhu, D., Hyun, S., Pignatello, J. J., & Lee, L. S. (2004). Evidence for π – π Electron Donor–Acceptor Interactions between π -Donor Aromatic Compounds and π -Acceptor Sites in Soil Organic Matter through pH Effects on Sorption. *Environmental Science & Technology*, 38(16), 4361–4368. <https://doi.org/10.1021/es035379e>
- Zhu, Z., Duan, W., Chang, Z., Du, W., Chen, F., Li, F., & Oleszczuk, P. (2023). Stability of Functionally Modified Biochar: The Role of Surface Charges and Surface Homogeneity. *Sustainability*, 15(10), 7745. <https://doi.org/10.3390/su15107745>

APPENDICES

Appendix I: Selected heavy metal concentration of water at tannery effluent disposal points.

Tannery	Selected HM (mg/L)	September			October			November			AQC
Site 1		1	2	3	1	2	3	1	2	3	
	Cr	0.066	0.043	0.052	0.554	0.002	0.002	<0.012	<0.015	0.100	0.268
	Ni	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.260
	Cu	0.018	<0.002	<0.002	0.012	<0.015	<0.002	0.000	0.000	<0.002	0.266
	Zn	0.059	<0.005	0.003	<0.005	<0.002	<0.005	<0.005	<0.005	<0.005	0.276
	Pb	<0.015	0.060	0.012	<0.015	<0.015	<0.015	<0.015	<0.015	0.032	0.270
Site 2											
	Cr	0.012	0.014	0.002	0.005	0.008	0.000	0.490	0.015	0.000	0.268
	Ni	0.007	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	0.260
	Cu	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	0.266
	Zn	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	0.276
	Pb	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	0.270
Site 3											
	Cr	6.010	6.082	6.215	6.892	6.000	6.722	5.852	6.000	5.435	0.268
	Ni	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.260
	Cu	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	0.266
	Zn	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	0.276
	Pb	0.052	0.014	0.016	0.015	0.063	0.058	0.021	0.015	0.015	0.270

Appendix II: Hawk Analysis Results Of Characterization Of Biochar.

SAMPLE ID	WEIGHT	S1	S2	S3	TOC	HI	OI	CC	AI	OSI
	(mg)				(wt.%)			(wt.%)		
Cal STD	61.6	0.08	7.34	0.45	2.85	256	15	0.17	2.35	2.00
Qty STD	61.4	0.08	6.66	0.42	2.85	234	14	0.18	2.33	2.00
Treated banana peels	100	80.98	104.1	23.60	33.25	313	70	0.65	27.27	243.00
Treated coffee husks	100	32.11	122.97	26.91	36.07	340	74	0.81	29.58	89.00
Treated coffee husks /Treated banana peels	100	64.04	98.46	24.74	33.79	291	73	0.71	27.7	189.00
non-treated coffee husks	100	34.65	95.72	57.53	36.76	291	156	1.69	30.15	94.00
Non-treated banana peels	100	63.26	107.36	28.03	34.35	312	81	0.44	28.17	184.00
non-treated coffee husks/non-treated banana peels	100	73.86	97.18	24.70	33.29	291	74	0.41	27.30	221.00

Appendix III: Chromium remediation at 20 minutes contact time.

	Initial Chrome Concentration (mg/L)	Contact Time(mins)	Final Concentration (mg/L)	Removal Percentage (%)
Treated banana peels	6.000	20	5.220	13.00
Treated coffee husks	6.000	20	4.800	20.00
Treated coffee husks +treated banana peels	6.000	20	4.980	17.00
non-treated coffee husks	6.000	20	3.606	40.00
non-treated banana peels	6.000	20	5.340	11.00
non-treated coffee husks+non- treated banana peels	6.000	20	5.400	10.00

Appendix IV: Chromium remediation at 40 minutes contact time

	Initial Chrome Concentration (mg/L)	Contact Time(m)	Final Concentration	Removal Percentage (%)
Treated banana peels	6.000	40	2.400	60.00
Treated coffee husks	6.000	40	1.680	72.00
Treated coffee husks +treated banana peels	6.000	40	2.100	65.00
Non-treated coffee husks	6.000	40	1.200	80.00
Non-treated banana peels	6.000	40	2.220	63.00
Non-treated coffee husks+non- treated banana peels	6.000	40	3.000	50.00

Appendix V: Chromium remediation at 60 minutes contact time.

	Initial Chrome Concentration (mg/L)	Contact Time(m)	Final Concentration	Removal Percentage
Treated banana peels	6.000	60	0.600	90.00
Treated coffee husks	6.000	60	0.264	95.60
Treated coffee husks +treated banana peels	6.000	60	0.480	92.00
Non-treated coffee husks	6.000	60	0.070	98.83
Non-treated banana peels	6.000	60	0.420	93.00
Non-treated coffee husks+non- treated banana peels	6.000	60	0.846	85.90

Appendix VI: Chromium remediation at 80 minutes contact time.

	Initial Chrome Concentration (mg/L)	Contact Time(s)	Final Concentration	Removal Percentage
Treated banana peels	6.000	80	0.586	90.23
Treated coffee husks	6.000	80	0.300	95.00
Treated coffee husks +treated banana peels	6.000	80	0.313	94.78
Non-treated coffee husks	6.000	80	0.121	97.98
Non-treated banana peels	6.000	80	0.326	94.56
Non-treated coffee husks+non- treated banana peels	6.000	80	0.600	90.00