

**DETERMINATION OF WATER QUALITY STATUS, REMEDIATION AND
SYNTHESIS OF MULTIWALLED CARBON NANOTUBE/HYDROCHAR
COMPOSITE IN RIVER KATHITA, MERU, KENYA.**

GLORY GATWIRI GITONGA

**A Thesis Submitted to the Graduate School in Partial Fulfillment of the
Requirement for the Award of the Degree of Master of Science in Chemistry of
Chuka University**


CHUKA UNIVERSITY

OCTOBER 2025

DECLARATION AND RECOMMENDATION

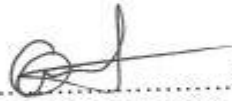
Declaration

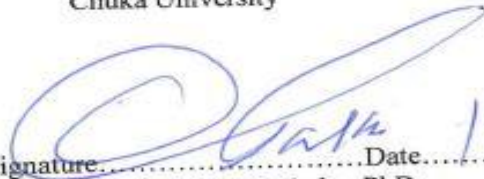
This thesis is my original work and has not been presented for an award of diploma or conferment of degree in any other University.

Signature..........Date.....19/10/25.....
SM11/57668/22
Glory Gatwiri Gitonga

Recommendation

This thesis has been examined, passed and submitted with our approval as University supervisors

Signature..........Date.....19/10/25.....
Prof. Joel Mwangi Gichumbi, PhD
Chuka University

Signature..........Date.....19/10/2025.....
Prof. Ochieng Ombaka, PhD
Chuka University



COPYRIGHT

©2025

All rights are reserved. No part of this thesis may be reproduced, stored in a retrieval system, including photocopying or transmitted in any form without permission in writing from the author or Chuka University.

DEDICATION

This thesis is dedicated to my lovely mother Mercy Kawira for her invaluable contribution through my academic journey.

ACKNOWLEDGEMENT

First, I would like to express my sincere thanks to my supervisors Prof. Ochieng Ombaka and Prof. Joel Mwangi Gichumbi for their tireless support, valuable criticism, encouragement, guidance and motivation throughout the period of this study. I also wish to appreciate Juliet Makau, Eric Lihanda, and for their guidance in UV-VIS and FTIR analysis. I am also grateful to the staff of the department of Geology and Mines for their support during data analysis, without forgetting the support is received from my course mates in terms of ideas and advice. May God bless you all. I thank Chuka University for giving me an opportunity to enroll for this course. The patience, encouragement and financial support given by my family members cannot go unacknowledged and is highly appreciated

ABSTRACT

Freshwater is required for life as well as several other activities such as human consumption, agricultural processes and industrial processes. Heavy metals are absorbed into water bodies through various pathways have adverse effect on the liver, kidneys, lungs, brain, and bones. This study sought to determine the physiochemical parameters, bacteriological, heavy metals and synthesize and characterize a composite of multi-walled carbon nanotubes (MWCNTs)/hydrochar of tea waste and utilize it for removal of Cu^{2+} ions from river Kathita. Tea wastes were collected from Meru tea factories and MWCNTs purchased from reputable suppliers. The tea waste samples were washed, dried and the MWCNTs, functionalized with sulfuric-nitric acid. The MWCNTs/hydrochar composite was characterized using FTIR and XRD. The water samples and sediments were collected in two seasons from River Kathita using grab method, transferred to 500 ml plastic bottles and transported to Chuka University Laboratory for analysis in a cooler box at 4°C . Standard methods for determining physicochemical and bacteriological parameters were employed and batch adsorption experiments were conducted to study the effect of pH, temperature, contact time, speed, initial metal concentration and dosage on adsorption of Cu^{2+} ions. The remaining copper (II) ions concentration was determined using AAS. The water turbidity, electrical conductivity, dissolved oxygen, nitrogen and phosphorous content, TDS and TSS were found to be high during the wet season compared to dry season. pH registered small changes to more neutral-alkaline during the wet season. The pH, temperature, conductivity, TDS, phosphorus and nitrates were within the guidelines by WHO in both seasons. Turbidity and TDO exceeded the WHO and KEBS guidelines in both seasons which indicated high amounts of organic matter. The total coliform counts and faecal coliforms during wet season were beyond proposed standards of safe recreational or agricultural use. This was due to extensive runoff as well as sewer discharge into the water during the rainy season. (MWCNTs) and hydrochar from tea waste composite had a big removal efficiency of 96.5% under optimum conditions. From the kinetic modeling, the adsorption process obeyed pseudo-second order reaction ($R^2 = 0.96683$) trend showing that the process is chemisorption driven. There was greater fit of the adsorption equilibrium data on Langmuir isotherm model ($R^2 = 0.99529$) indicating monolayer surface coverage of Cu^{2+} ions by homogenous surface. There was a high regeneration potential of the absorbed Cu^{2+} ions being efficiently desorbed. The MWCNTs/hydrochar composite is highly effective and sustainable since it can be recycled multiple times without the loss of functionality on a significant scale. The addition of Pb^{2+} ions did not drastically influence the removal of Cu^{2+} while addition of Cd^{2+} ions and the binary solution of Pb^{2+} and Cd^{2+} caused a significant decrease in the efficiency of copper adsorption. The MWCNTs/hydrochar composite is generally a sustainable option for enhancing the quality of the polluted rivers' water.

TABLE OF CONTENT

DECLARATION AND RECOMMENDATION	ii
COPYRIGHT	iii
DEDICATION.....	iv
ACKNOWLEDGEMENT.....	v
ABSTRACT.....	vi
TABLE OF CONTENT.....	vii
LIST OF TABLES	xi
LIST OF APPENDICES	xiii
LIST OF ABBREVIATIONS AND ACRONYMS	xiv
CHAPTER ONE: INTRODUCTION	15
1.1 Background Information.....	15
1.2 Statement of the Problem.....	18
1.3 Objectives	19
1.3.1 General Objective	19
1.3.2 Specific Objectives	19
1.4 Research Questions.....	20
1.5 Significance of the Study	20
CHAPTER TWO: LITERATURE REVIEW.....	21
2.1 Introduction.....	21
2.2 Physicochemical Parameters.....	22
2.2.1 Water Temperature	22
2.2.2 Water pH.....	22
2.2.3 Water Turbidity.....	22
2.2.4 Water Electrical Conductivity.....	23
2.2.5 Water Total Dissolved Solids	23
2.2.6 Water Dissolved Oxygen	24
2.2.7 Water Phosphates.....	24
2.2.8 Water Nitrates	25
2.2.9 Heavy Metals	25
2.3 Bacteriological Properties.....	26

2.4 Carbon nanotubes.....	26
2.5 Hydrochar of tea waste (HTW).....	27
2.6 Techniques used for the removal of Heavy Metals from Water.	28
2.6.1 Adsorption.....	29
2.6.2 Use of Tea wastes as Adsorbent for Heavy Metal Adsorption.....	29
2.7 Removal of Heavy Metals Using Multiwalled Carbon Nanotubes (MWCNTS).....	30
2.7.1 Regeneration of Adsorbent	30
2.8 Theoretical Framework.....	31
2.8.1 Fourier Transform Infrared Spectroscopy (FTIR)	31
2.8.2 X-ray diffraction (XRD)	31
CHAPTER THREE: MATERIALS AND METHODS	33
3.1 Study Area	33
3.2 Research design	33
3.3 Sample size	34
3.4 Materials	34
3.4.1 Reagents.....	34
3.4.2 Apparatus	34
3.5 Water Sample Collection	35
3.6 Water Sample Preparation	35
3.6.1 Water Temperature	35
3.6.2 Water pH.....	35
3.6.3 Water Turbidity.....	35
3.6.4 Water electrical Conductivity	35
3.6.5 Water Total Dissolved Solids	36
3.6.6 Total Dissolved Oxygen (DO).....	36
3.6.7 Phosphates.....	36
3.6.8 Nitrates.....	37
3.6.9 Heavy Metals	37
3.6.10 Bacteriological Analysis	37
3.7 Heavy Metals Adsorption	38
3.7.1 Oxidation of Multiwalled Carbon Nanotubes.....	38

3.7.2 Dispersion of Multiwalled Carbon Nanotubes.....	38
3.7.3 Tea waste collection.....	38
3.7.3.1 Surface Functionalization of the Tea waste	38
3.7.4 Preparation of hydro char of tea waste.....	39
3.7.4.1 Tea Wastes/Multiwalled Carbon Nanotubes Composite	39
3.8 Characterization of the Adsorbents.....	39
3.8.1 Structural Analysis.....	39
3.8.2 Adsorption Experiments	39
3.8.3 Desorption and Regeneration of Adsorbent.....	40
3.9 Optimization of Parameters in Adsorption Process	41
3.9.1 Effect of Contact Time.....	41
3.9.2 Effect of pH.....	42
3.10 Interference Studies	42
3.11 Data Analysis and Presentation	42
3.12 Ethical Considerations	43

CHAPTER FOUR: RESULTS AND DISCUSSION..... 44

4.1 Physical and Chemical Parameters	44
4.1.1 Physicochemical Parameters During Wet and Dry Seasons.....	44
4.1.2 Comparison of physicochemical Parameters during Wet and Dry Season with other Studies.....	48
4.1.3 Heavy metals and Sediments in river Kathita during Wet and Dry Seasons	51
4.1.4 Comparison of Lead, Copper and Cadmium in Surface Water in Dry and Wet Season.....	57
4.2 Bacteriological Analysis of River Kathita during Wet and Dry Season.....	59
4.2.1 Total Coliforms.....	59
4.2.2 Faecal Coliform	61
4.2.3 Relationship between Bacteriological Parameters and Physicochemical Parameters.....	62
4.3 Characterization of the Adsorbents.....	65
4.3.1 FTIR Spectra of Tea Waste Hydrochar/MWCNTs Composite	65
4.3.2 XRD Spectra of Tea Waste Hydrochar/MWCNTs Composite	68
4.4 Adsorption Experiments of Copper (II) Ions	71

4.4.1 Effect of Adsorbent Dosage on Adsorption of Cu (II) Ions.....	71
4.4.2 Effect of Initial Metal Concentration on Adsorption.....	74
4.4.3 Effect of Contact Time on Adsorption of Cu (II) Ions	75
4.4.4 Effect of Temperature on Adsorption of Cu (II) ions	76
4.4.5 Effect of pH on Adsorption of Cu (II) ions.....	77
4.5 Kinetic Studies for Adsorption of Cu (II) ions	78
4.6 Adsorption Isotherms for Cu (II) Ions	80
4.7 Desorption of Cu (II) Ions from Adsorbent Surface	82
4.8 Effects of Cations Interference on Adsorption of Cu (II) Ions	83
CHAPTER FIVE: SUMMARY, CONCLUSION AND	
RECOMMENDATIONS	85
5.1 Summary	85
5.1.1 Physicochemical Parameters.....	85
5.1.2 Biological Parameters	86
5.1.3 Adsorption Studies.....	86
5.1.4 Desorption Studies	87
5.1.5 Interference Studies	87
5.2 Conclusion	87
5.3 Recommendations.....	88
5.4 Suggestions for Further Studies	88
REFERENCES.....	89
APPENDICES	108

LIST OF TABLES

Table 1: Physiochemical parameters of river Kathita during dry season	44
Table 2: Physiochemical parameters of river Kathita during the wet season.....	45
Table 3: Levels of lead in sediment and surface water during dry and wet season.....	52
Table 4: Levels of copper in sediment and surface water during dry and wet season.....	53
Table 5: Levels of cadmium in sediment and surface water during dry and wet season.....	55
Table 6: Total coliforms during wet and dry seasons.....	60
Table 7: Total faecal coliforms during wet and dry season.....	61
Table 8: Spearman correlation coefficients for physical parameters during dry season	63
Table 9: Spearman correlation coefficients for physical parameters during wet season.....	64
Table 10: Pseudo first and second order kinetics constants for Cu (II) ions adsorption	79
Table 11: Freundlich and Langmuir constants for adsorption of Cu (II) ions	81

LIST OF FIGURES

Figure 1: Schematic structure of (a) MWCNT (b) SWCNT (Zhao & Stoddart, 2009).....	27
Figure 2: Area Map (surveys maps of Kenya).....	33
Figure 3: Comparison of lead, copper and cadmium in surface water in dry and wet season.....	57
Figure 4: Comparison of lead, copper and cadmium in sediment in dry and wet season.....	58
Figure 5: FTIR spectrum of hydrochar of tea waste/MWCNTs composite A.....	65
Figure 6: FTIR spectrum of hydrochar of tea waste/MWCNTs composite B.....	66
Figure 7: FTIR spectrum of hydrochar of tea waste/MWCNTs composite C.....	67
Figure 8: XRD spectrum of hydrochar of tea waste/MWCNTs composite A.....	68
Figure 9: XRD spectrum of hydrochar of tea waste/MWCNTs composite B.....	69
Figure 10: XRD spectrum of hydrochar of tea waste/MWCNTs composite C.....	70
Figure 11: Effect of adsorbent dosage on adsorption of Cu (II) ions (composite A).....	71
Figure 12: Effect of adsorbent dosage on adsorption of Cu (II) ions (composite B).....	72
Figure 13: Effect of adsorbent dosage on adsorption of Cu (II) ions (composite C).....	73
Figure 14: Effect of initial metal concentration on adsorption of Cu (II) ions.....	74
Figure 15: Effect of contact time on adsorption of Cu (II) ions.....	75
Figure 16: Effect of temperature on adsorption of Cu (II) ions.....	76
Figure 17: Effect of pH on adsorption of Cu (II) ions.....	78
Figure 18: Pseudo first order kinetics of Cu (II) ions adsorption.....	79
Figure 19: Pseudo second order kinetics of Cu (II) ions adsorption.....	80
Figure 20: Freundlich isotherm of Cu (II) ions adsorption.....	81
Figure 21: Langmuir isotherm of Cu (II) ions adsorption.....	82
Figure 22: Percentage desorption of Cu (II) ions.....	83
Figure 23: Cation interference on adsorption of Cu (II) ions.....	84

LIST OF APPENDICES

Appendix 1: Pseudo first and second order kinetic data.....	108
Appendix 2: Langmuir and Freundlich isotherm data	109
Appendix 3: National Commission for Science, Technology & Innovation (NACOSTI) Research Permit.....	110

LIST OF ABBREVIATIONS AND ACRONYMS

AAS:	Atomic Absorption Spectrophotometer
CNTs:	Carbon nanotubes
DO:	Dissolved Oxygen
FE-SEM:	Field emission scanning electron microscopy
FTIR:	Fourier Transform Infrared
HTC:	Hydrothermal carbonization
HTW:	Hydro char Tea Waste
ICPMS:	Inductively Coupled Plasma Mass Spectrometry
ICP-OES:	Inductively Coupled Plasma Optical Emission Spectroscopy
KEBS:	Kenya Bureau of Standards
MWCNTs:	Multiwalled carbon nanotubes
NEMA:	National environmental management agency
SDBS:	Sodium dodecyl benzene sulfonate
SDG:	Sustainable Development Goal
SEM:	Scanning Electron Microscopy
SWCNTs:	Single walled carbon nanotubes
TDS:	Total Dissolved Solids
XRD:	X-rays diffraction

CHAPTER ONE

INTRODUCTION

1.1 Background Information

Water is an important natural resource as it supports life development and human activities. In the entire planet, 97% of water is salty and the remaining 3% is fresh water (Cassardo & Jones, 2011). Planets freshwater constitute of 70% Greenland icecaps and the rest is found deep underground (Hasanuzzaman *et al.*, 2019). The decline in fresh water has been caused by population increase, urbanization, industrialization and concentrated agricultural actions and therefore, monitoring water resources regularly is needed to access the quality of water for ecosystem health and hygiene, industrial, agricultural and domestic purposes (Poonam *et al.*, 2013). The quality of water describes the condition of water including chemical, physical and biological with respect to its suitability depending on the purpose (Achieng' *et al.*, 2017).

Water quality is affected by the physiochemical parameters based on their levels that are influenced by seasonal variation, volcanic eruptions, urbanization and anthropogenic activities like agricultural runoff (Likambo, 2014). Levels of this parameters above the permissible standards by World Health Organization (WHO) pollute the water making it unsafe for human consumption (Aturamu, 2012). Biological properties entail microbes or microbiological contaminants (Shmeis, 2018). Water naturally contains a wide variety of microorganisms like Salmonella, typhus, cholera, and shigella bacteria, among others Helminths like Guinea, hookworms, and roundworms, as well as viruses like polio, hepatitis A, meningitis, and encephalitis. Fecal matter may also include *E. coli*, fecal coliform bacteria, and total coliform bacteria (Aladese & Pondei, 2021). High levels microbiological contaminants may be attributed to untreated municipal sewage runoff, leaching of waste from latrines and runoff from animal waste which can cause waterborne diseases to human being (Odada *et al.*, 2003).

Water quality issues in developed countries include anthropogenic activities, volcano activities, heavy metals, residue from urban, natural mixtures and agricultural waste sources. Agricultural nations like Brazil, China, India have high risk of water contamination leading to poor health (Darwall *et al.*, 2018). People in developed

countries have large cases of diseases associated with consumption of contaminated water, inadequate water supply and sanitation (Bartram *et al.*, 2005). Every year, 1.8 million people, largely children, die in underdeveloped nations from drinking contaminated water (Prüss-Üstün *et al.*, 2016). A recent study carried out on river Kathita by Gitonga (2021), showed that river Kathita contains high levels of phosphates and nitrates. High levels of nitrates and phosphates in water bodies fasten the growth of aquatic plants creating negative effect on water quality by accelerating the growth of algae clump, bad odor and decoloration. Excessive growth of aquatic life can lead to problems in navigation and aeration. Further, dead phytoplankton and macrophytes settle at the bottom of the water bodies which leads to microbial growth thrives and utilization of dissolved oxygen to degrade the organic waste. The deficiency of oxygen contributes to the death of aerobic plants and microbes which causes suffocation in fish and other aquatic organisms (Singh, 2013).

Another study carried out on river Kathita by Muriithi and Yu (2015), showed that TDS, electrical conductivity and salinity were high in areas with intensive horticulture. They were traces of cadmium, phosphates and zinc mainly due to application of phosphate-based fertilizers especially among large scale intensive horticultural sites. Nitrates levels were high in areas with small scale intensive horticulture and agriculture due to use of farmyard manure.

These researches are limited to chemical and physical properties and some heavy metals of water in river Kathita with little information on other heavy metals like lead, copper and biological properties and an appropriate and affordable way to get rid of them. This calls for research on heavy metals and an appropriate and cost-effective way of getting rid of contaminants. Since river Kathita runs alongside the town of Meru, therefore either unintentionally or on purpose, waste water from garages and carwashes is discharged into the river which may contribute to presence of heavy metals. Numerous agricultural activities and the use of fertilizers in the upper reaches of the River Kathita contribute to the presence of nitrates and phosphates in the water. Heavy metals including Pb, Cd, Cu, Zn, Ni, Cr, and metalloids like as in drinking water have negative effects on human health such as allergies, hyperpigmentation, skin lesions, skin cancer, neurological damage, hypertension, cardiovascular illness, and pulmonary disease

(Hashmi *et al.*, 2014). Runoff or seepage from fertilized agricultural lands, municipal and industrial waste water, garbage dumps, animal feedlots, septic tanks and private sewage disposal systems, urban drainage, and decomposing plant matter can all be sources of nitrogen and nitrates (Dey *et al.*, 2021).

To tackle water contamination, numerous countries have implemented increasingly stringent regulations. A key challenge today is the effective removal of heavy metal ions from surface water. Precipitation followed by coagulation has been widely utilized to remove hazardous metals from water. However, using this process frequently yields huge amounts of sludge with very low levels of heavy metals (Joseph *et al.*, 2019). Although membrane filtration is a tried- and-true technique for eliminating metal ions, its high cost prevents it from being utilized generally. The use of bio sorbents has been recommended as being less expensive, more efficient, and reducing chemical and biological sludge. Our environment contains a variety of biosorbents that can remove heavy metals from surface water (Khulbe & Matsuura, 2018).

Traditional adsorbents are used to remove heavy metals from water, but their efficiencies and sorption capacity limit their use. To overcome the challenges of using conventional sorbents, nanomaterials are currently being used as new adsorbents for the adsorption of toxic metals from water. Because of their non-toxic nature and high sorption capacity, carbon-based nanomaterials with graphene oxide, fullerenes, and carbon nanotubes have been widely used, particularly for heavy metal removal from wastewater (Kumar, 2023). In this study adsorption of heavy metals using hydro char of tea waste and multiwalled carbon nanotube composite will be studied. The demand for tea is rising dramatically on a global scale and will do so during the coming ten years as well (Hayat *et al.*, 2015).

Hydrochar has porous structure and abundant surface functional groups that depends on the feed-stock and treatment conditions (Paneque *et al.*, 2017). Studies have shown that hydro char can be effectively applied to use in water treatment in a wide variety of pollutants like heavy metal and dyes (Ighalo *et al.*, 2022). As a result of the sharp increase in global tea production necessary to fulfill this growing demand, there are significant environmental problems as a result of the massive volumes of waste tea is

produced. In some studies, eggshells, olive mill waste, peanuts, pistachio shells, sugar beet bagasse and sunflowers have been used as the waste to remove heavy metals from waters. Every year, enormous amountsof tea waste, a type of agricultural waste, are produced all over the world. It is estimated that organic solid waste from tea processing to be 486.47 kilograms per month and inorganic solid waste to be 15.38 kilograms per month (Mukhwana, 2019). It's interesting to note that tea waste has an insoluble cell wall made of cellulose, lignin, tannin, and structural proteins with certain functional groups that can form physicochemical interactions with heavy metals and other pollutants, removing dangerous materials from solutions (Thakur & Parmar, 2013).

The maximum adsorption capacities using tea waste were much better than other materials being used and calculated as 1.197, 1.457, 1.163 and 2.468 mg/g, for Pb, Zn, Ni and Cd, respectively (Dey *et al.*, 2021). This study seeks to assess the need to improve water quality of river Kathita for domestic and agricultural use and also to determine feasibility of low cost hydrochar nanocomposite from tea waste adsorbent which is safe for environment, having a good ability to regenerate and effective as a treatment technology. The isothermal behavior and adsorption kinetics will be investigated in batch mode using UV-Visible spectroscopy. The equilibrium isotherm data will be fitted to the Langmuir and Freundlich equations, and isotherm equation constants will be determined. The kinetics of adsorption will be studied using pseudo-first order and pseudo-second order principles.

1.2 Statement of the Problem

River Kathita, in Eastern Kenya flows through agricultural lands with intensive agricultural activities due to the rich volcanic soils. It also flows through urban areas (Meru Town) which has industrial activities, from where there are possible sources of environmental and water pollution. Meru Town is a fast-growing town in terms of industrialization and a rapid increase in population. Most of the household around Meru region get their water from River Kathita. Volcanic soil around the river contains some contaminants that finds its way to the river through runoff. Agricultural activities such as the use of pesticides, insecticides, weed killers, and commercial fertilizers result in water pollution due to runoff into the river therefore increasing the levels of heavy metals. There are many industries around Meru such as tea, food processing and textile

industries that discharge their effluents into the environment increasing pollution. The high population in Kathita River ecosystem results in contamination from fecal matter, effluent from car washes and petrol stations. There has been a reported increase in the number of non-communicable diseases such as cancers and kidney disorders in the Kathita River Ecosystem. Heavy metals can pose a risk to both animal and human health since they are toxic, non-biodegradable and easily enter the food chain. The pollution of water due to microbial pathogens has led to the report of waterborne diseases such as cholera and typhoid. The pollution from anthropogenic and other activities necessitates the development of better methods of water treatment and purification. The current methods being employed for water treatment are costly, which cannot be implemented by the less privileged in the society. Adsorption has been shown to be one of the most reliable and cost-effective methods. The use of nanomaterials with enhanced surface area will enhance the adsorption capabilities of locally available material and can easily be synthesized. Therefore, there is the need to come up with alternative methods of adsorption which can utilize nanomaterials materials composited with modified available waste materials such as tea waste that are environmentally friendly, have high ability to regenerate and cost-effective materials for water remediation.

1.3 Objectives

1.3.1 General Objective

To determine physicochemical, bacteriological properties and removal of selected heavy metals using multiwalled carbon nanotubes/hydrochar of tea waste composite in River Kathita during dry and wet season.

1.3.2 Specific Objectives

- i. To determine physicochemical properties (Temperature, pH, Turbidity, Conductivity, TDS, TDO, Phosphates, Nitrates) from river Kathita and heavy metals (Cu, Pb and Cd) from sediment and water both during dry and wet season.
- ii. To determine bacteriological properties (Total coliform and Faecal coliform) of water samples from river Kathita during dry and wet season.
- iii. To synthesis and characterize multiwalled carbon nanotubes/hydrochar of

tea waste composite.

- iv. To determine the kinetics and thermodynamics of removal of heavy metals (Pb, Cd and Cu) using multiwalled carbon nanotubes/hydrochar of tea waste composite and its ability to regenerate.

1.4 Research Questions

- i. What is the difference between the physiochemical parameter levels during the wet season and dry season in River Kathita?
- ii. What is the difference between bacteriological parameters levels during wet and dry season in River Kathita?
- iii. Can a composite of multiwalled carbon nanotubes/tealeaves waste be synthesized and characterized?
- iv. What are the kinetics and thermodynamics of removal of heavy metals (Pb and Cu) using multiwalled carbon nanotubes/hydrochar of tea waste composite and its ability to regenerate?

1.5 Significance of the Study

This study will provide information about the physicochemical and bacteriological properties and heavy metals of water from river Kathita and their levels during dry and wet seasons. This is due to variation in levels depending on the region the sample is taken from and the season. The study is of importance because its finding will contribute to additional knowledge in the existing research. The study will provide information about the status of water quality in River Kathita and remediation techniques that can be used in minimizing levels of heavy metals to policy makers like National Environmental Management Authority (NEMA). This information helps guide relevant stakeholders who might be interested in provision of water to residents of Meru Town and its surroundings. The study will be able to create awareness of the danger involved in utilizing untreated water from River Kathita in which upon implementation the number of people being affected by diseases due to water directly or through human chain will be minimized hence reducing the number of people visiting health center for treatment. The industrialist can use the prototype to develop a version which can be utilized in a large scale for removal of heavy metal and bacteriological contaminants utilizing available tea waste.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

Water is important and necessary for our daily lives and life-sustaining activities. As a result, in order to check the quality of water for its safety and acceptability, a number of tests must be performed in accordance with water quality standards to determine the concentration of various components (Inglezakis *et al.*, 2016). Human activities such as manufacturing, agriculture and industrialization continue to pollute drinking water sources.

Water Pollution occurs when waste materials such as synthetics or microorganism move down the stream, waterway, lake affecting the quality of water and making it unworthy for human consumption (Juneja & Chaudhary, 2013). Everything that occurs in a water catchment area is reflected in the quality of the water that flows through it, because the results of human activity and lifestyle eventually end up in rivers via runoff (Lintern *et al.*, 2018). The likelihood of water-related diseases rises when people in developing nations do not consistently have access to an improved source of drinking water. The WHO estimates that 1.6 million people die annually from water-related illnesses like diarrhea, with 90% of these deaths occurring in children under the age of five (Lee *et al.*, 2020).

Heavy metals are the priority contaminants because their evolution, even at low levels, is unknown (Pontoni, 2016). The use of heavy metal-containing compounds for domestic and agricultural purposes, such as using fertilizer, eating tainted food, and smoking cigarette are sources of heavy metal contamination. Industrial activities such as burning coal and petroleum products in power plants are another source, as well as mining and smelting operations (Njuguna *et al.*, 2017). The most popular technique for elemental analysis is atomic absorption spectrometry (ASS), but it has lower precision than inductively coupled plasma methods (ICPMS) and graphite furnace atomic absorption spectrophotometry. When compared to other methods of elemental analysis, ICPMS has a higher detection limit and can be used for multielement analysis (Planeta *et al.*, 2021). Using a technique with low precision could result in a false conclusion that certain contaminants are not present in water bodies (Gajek *et al.*, 2013).

2.2 Physicochemical Parameters

Water is the most important resource in a river ecosystem, and its assessment is determined by its physical and chemical properties. Physical examination entails determination of water temperature, light, turbidity, how clear the water is and total dissolved solids among others. Chemical examination entails determination of Dissolved Oxygen (DO), nutrient concentration, pH, total dissolved solids, electrical conductivity and alkalinity among others.

2.2.1 Water Temperature

Water temperature is affected by seasons, geographical location, and meteorological conditions such as rainfall, humidity, cloud cover, wind velocity, and turbidity (Mathew *et al.*, 2017). The guideline levels of water temperature recommended for drinking water by WHO are between 23-30 degrees Celsius (Mgbemena *et al.*, 2012).

According to Gitonga (2021), decrease in temperature in the upper part of river Kathita is attributed to its closeness to Mt Kenya where the water mainly results from melting ice having low temperature. On the other hand, increased temperature in the town area is attributed to agricultural activities, clearing of vegetation and discharge of heat effluent from Meru town.

2.2.2 Water pH

The pH value of water is used to determine its acidity or alkalinity (Gopalkrushna, 2011). It has an impact on water quality affecting metal solubility, alkalinity, and hardness. The standards recommended for drinking water is pH range of 6.5-8.5 (World Health Organization, 2002). Higher pH values during dry seasons may be due to increased photosynthesis blooms of cyanobacteria and other algae leading to precipitation of carbonates and bicarbonate. Lower pH values are attributed to the influx of acidic waste entering rivers from factories and industries (Ombaka & Gichumbi, 2012). Acidic water has low pH values and can cause gastrointestinal problems such as hyperacidity and ulcers in humans (Buridi & Gedala, 2014).

2.2.3 Water Turbidity

Water turbidity rises as a result of light penetration interference that affect the color of water and promotes microbial proliferation which harm aquatic life and affects surface

water quality (Mbura, 2018). Lower turbidity is related with the dry seasons while higher turbidity is connected with the rainy seasons. The main cause of turbidity is the deposition of silt into the aquifer. Studies have shown that drinking water with a high turbidity level increases the risk of developing diseases of the liver, thyroid, skin, and eyes, as well as other changes to the immune and reproductive systems (Kodavanti & Loganathan, 2017). According to Kenya Bureau of Standards KEBS (2010), the permissible guideline for turbidity is 5 NTU

2.2.4 Water Electrical Conductivity

Water electrical conductivity (EC) is affected by the concentration of conductive ions like inorganic dissolved solids in the water (EPA, 2014). Electrical conductivity reflects water mineralization and varies according to the concentration of dissolved salts. It is frequently influenced by temperature because it acts on salt dissolution in water (Benrabah *et al.*, 2016). EC also entails a measure of salinity that affects the taste of water and shows the presence of dissolved ions, increase in ionizable salts in water that leads to higher EC of the water (Jain & Agarwal, 2012). The water is safe to drink if the conductivity values are less than 1000 s/cm (World Health Organization, 2002).

2.2.5 Water Total Dissolved Solids

Total Dissolved Solids (TDS) is a measure of the dissolved combined content of all inorganic and organic substances present in a liquid in molecular, ionized or micro-granular suspended form. Water can dissolve a wide variety of inorganic and organic minerals and salts, including potassium, calcium, sodium, bicarbonates, chlorides, magnesium, and sulphates. These minerals produce an unpleasant taste and dilute the color of the water (Gichuki & Gichumbi, 2012). Increased TDS in water can be attributed to surface run-off like the inorganic and organic minerals and salts which leads to hard water that is unfit for consumption (Otieno *et al.*, 2012). High levels of TDS are also undesirable for industrial application especially in food production as they can alter the flavor and appearance of final products and produce scales, speed up corrosion, precipitate foaming in boilers, and precipitate foaming (Sarda & Sadgir, 2015). According to World Health Organization (2002), the recommended value of TDS in water is, 1000 mg/L but however there is no health-based guidelines for TDS in Kenya up to date.

2.2.6 Water Dissolved Oxygen

Dissolved oxygen (DO) changes rapidly as a result of various environmental factors such as temperature elevation, water flow rate, aeration of the water as it tumbles over rocks, the chemical nature of bottom sediments, and as a product of photosynthesis by submerged aquatic plants and microbial life (Cronk & Fennessy, 2016). Low DO levels in rivers can be attributed to higher temperature, increased organic matter in rivers and increased microbial communities in river (Bora & Goswami, 2017). Low oxygen levels in water are also due to corrosion of chemical substances which makes the level of temperatures to rise. A sufficient amount of oxygen in the water provides a safe haven for bacteria and other pathogens that are anaerobic and harmful to human health (Rajiv *et al.*, 2012). The guidelines level of DO recommend for drinking water by WHO is above 6 mg/l.

2.2.7 Water Phosphates

Phosphates enter waterways from man-made sources such as human sewage, agricultural run-off from crops, sewage from animal feedlots, vegetable and fruit processing, chemical and fertilizer manufacturing, and detergents. The addition of large amounts of phosphates to waterways accelerates algae and plant growth in natural waters, increasing eutrophication and depleting the water body of oxygen (Otieno, 2015). Clean water for drinking should contain low levels of phosphate. Therefore, high levels of phosphate indicate water contamination (Ombaka *et al.*, 2013a).

According to Gitonga (2021), high levels of phosphate is attributed to increased agricultural activities in a given area involving the use of agricultural chemicals (Orina *et al.*, 2017). In a study carried by Chebet *et al.* (2020), the levels of phosphates in the study ranged from 0.13 to 11.06 mg/L which was above the WHO permissible limit (World Health Organization, 2002). The sources of phosphates in this study are attributed to excess use of fertilizers in farms and anthropogenic sources like phosphates rocks. Phosphates are moderately soluble and not very mobile in soils but their transportation through surface runoff and soil erosion can increase their solubility in surface water (Nieder *et al.*, 2018). The WHO permissible limit of phosphate in drinking water is 0.5 mg/L (World Health Organization, 2002).

2.2.8 Water Nitrates

Nitrates are an essential nutrient for the growth, reproduction, and survival of microorganisms (Tyagi *et al.*, 2018). The main sources of nitrate in water are animal and human waste, industrial effluent, and the use of chemicals, fertilizers, and silage through drainage systems (Shruthi & Anil, 2018). Nitrates may also enter water through surface runoff from surrounding catchment areas, effluent from point and non-point sources, dead animal cells, agriculture. Because of the heterocyst, cyanobacteria are responsible for the majority of nitrate fixation in freshwater systems (Otieno, 2015). Nitrate is highly soluble in water and can easily move through streams and ground water (Sewe, 2013). Excessive nitrate consumption can impair oxygen transport in the bloodstream. Infants under the age of four months lack the enzyme required to correct this condition known as methemoglobinemia, also known as blue baby syndrome (Sellami *et al.*, 2020). A study by Akubuenyi *et al.* (2013), reported high nitrates levels which was attributed to runoffs from near surface soils that causes high microbial load. The levels reduced in rainyseason due to high solubility. Another study by Gebre *et al.* (2016), also reported that, high nitrates level attributed to eutrophication that can make water become toxic to animals and humans leading to loss of species diversity.

2.2.9 Heavy Metals

Heavy metals accumulate in the biota every time they are ingested and are reserved more than they are assimilated then released into the surrounding. The toxicity of some metals in the aquatic environment such as zinc, copper, and cadmium increase the risk of them entering living system directly or indirectly causing serious health problems (Chen *et al.*, 2016). Long term exposure to zinc, copper, and cadmium causes health problems such as physiological problems with blood production and liver malfunction. In addition, zinc and cadmium intake through food and water may result in metal poisoning (Pandey & Madhuri, 2014). Heavy metal accumulation in aquatic ecosystems can be caused by emissions from rapid industrialization, mine tailings, untreated waste seepages containing toxic metals, as well as metal chelates from various industries, such as tanneries, steel plants, battery industries, thermal power plants, sewage sludge, application of heavy metal containing fertilizers, pesticides, insecticides, herbicides in agriculture, coal combustion residues (Mohiuddin *et al.*, 2022). Heavy metals prevent

some enzymes from performing their functions, which prevents the formation of haem, the pigment that combines with protein to form hemoglobin, in the bone marrow. Children who consume lead can develop brain damage (Christine *et al.*, 2018).

2.3 Bacteriological Properties

Bacteria are microscopic microorganisms that live in a variety of environments and differ in morphological aspects that depict their physical characteristics (Yang *et al.*, 2016). The three types of bacteria—spherical, rod, and spiral—can be distinguished by dividing cultures based on morphological traits like color, rate of growth, and colony texture as well as by using a microscopy technique (Petersen & McLaughlin, 2016). The main source of bacterial pollution in water is the excreta of warm-blooded animals such as humans, domestic and wild animals, and birds. The Coliform group, some subgroups of faecal streptococci, and other lower life form organisms are the most common (Rodrigues & Cunha, 2017). According to the WHO, no faecal coliform should be present in 100ml of drinking water. The main bacteria of concern in contaminated water are Salmonella species, Shigella species., E. coli, and Vibrio cholera, and the presence of coliforms has been widely used (Abila *et al.*, 2012). Infants and young children, people who are disabled or living in unsanitary conditions, the sick, and the elderly are the most vulnerable to waterborne disease (Githinji, 2019). Bacteriological contaminants are responsible for a wide range of diseases, including dysentery, typhoid fever, cholera, and gastroenteritis (Gemmell & Schmidt, 2013).

According to a study by Abila *et al.* (2012), Salmonella, E coli, Vibrio, Listeria, Staphylococcus aureus, Enterobacter, Klebsiella, and Pseudomonas were found in boreholewater in Kitui County, Kenya. A study conducted by Nyongesa *et al.* (2016), and Augustyn *et al.* (2016), indicates that Escherichia coli is the dominant microbe in river water, while other microbes such as Salmonella, Vibrio, Staphylococcus, and Klebsiella are not found in the majority of river water.

2.4 Carbon Nanotubes

Carbon nanotubes are among the types of allotropes of carbon which has an atomic number of 6 and plays a vital role in nanotechnology (Mubarak *et al.*, 2016). They were discovered accidentally by Iijima in 1991 while studying the surface of graphite

electrode used in electric discharge and since that time have developed into their own research (O'connell, 2018). Carbon nanotubes are classified into two types: single walled carbon nanotubes (SWCNTs) and multi walled carbon nanotubes (MWCNTs). SWCNTs has a diameter ranging from 0.7-2.5nm while for MWCNTs it ranges from 4-150nm. MWCNTs are made up of tens of graphitic layers with interlayer spacing ranging from 0.34 to 0.39 nm (Eatemadi *et al.*, 2014). The unique structure of CNTs make them have a remarkable property such as large surface area to volume ratios, high aspect ratios, low densities, high mechanical and tensile strengths, high electric and thermal conductivity, strong non-linear optical property, high absorbency, and antimicrobial property (Rashko *et al.*, 2022).

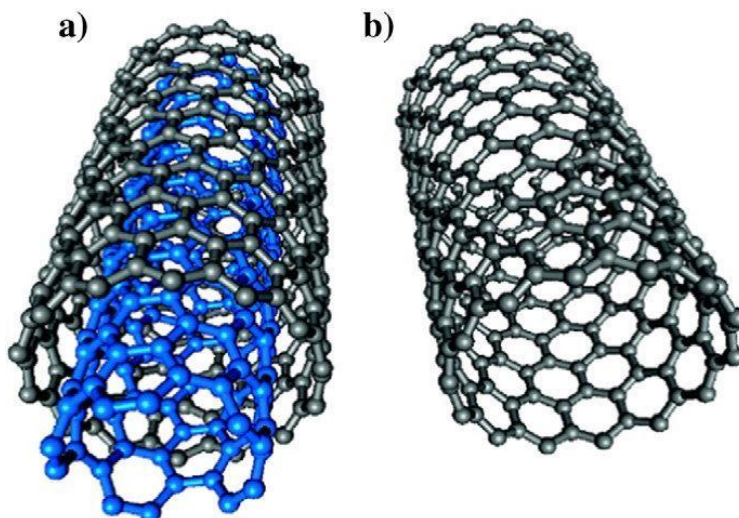


Figure 1: Schematic structure of (a) MWCNT (b) SWCNT (Zhao & Stoddart, 2009).

2.5 Hydrochar of Tea Waste (HTW)

Hydrochar is the hydrothermal carbonized of carbon rich biomass in the presence of water which leads to production of a solid material (Li & Wu, 2019). Hydrothermal carbonization (HTC) is an environmentally friendly solid waste treatment in which thermochemical conversion technology for biomasses that takes place in sub-critical water at temperatures of 120-300 C and pressures of 2-10 MPa (Zhuang *et al.*, 2019). HTC produces carbon-concentrated solids (hydro char), liquid (bio-crude), and gases (primarily CO₂), with typical yields of 45-70%, 5-25%, and 2-5% of the wet biomass weight, respectively (Kambo & Dutta, 2015). Hydrochar is some porous material rich in oxygenated functional groups, making it suitable for applications such as waste

water treatment absorbents, soil amelioration, catalysts, and super capacitor production (S. Zhang *et al.*, 2019). It is important to use carbon-containing materials released as waste after industrial processes in production of biomass-based adsorbent which helps in preventing environmental pollution (Kızıldağ, 2024). HTC is characterized by large specific surface area and rich void and structure which is very efficient adsorbent for various organic pollutants and heavy metals (Shi *et al.*, 2022). Literature reviews that hydrochar can be utilized as adsorbent in removal of heavy metals from industrial effluents due to availability of oxygen and nitrogen functionalities on the surface. Further, certain amount of nitrogen containing surface functional group on hydrochar can have a better adsorption performance than ordinary one (Lei *et al.*, 2018).

2.6 Techniques used for the Removal of Heavy Metals from Water

Heavy metal-contaminated water has been treated using various techniques in order to safeguard humans, living organisms, and the environment from the harmful effects of toxic heavy metals such as lead and improve water quality for domestic purposes. Various methods have been used for treatment of heavy metals such as ion exchange, chemical precipitation, membrane filtration, coagulation and flocculation, flotation and adsorption method. Although these methods can be used to remove heavy metals, each has its own set of advantages and disadvantages (Kurniawan *et al.*, 2006).

Ion exchange is costly and cannot be used to treat large amounts of water containing low concentrations of heavy metals, it is non-selectivity and has a high sensitivity to the pH of the aqueous solution making it less effective (Fu & Wang, 2011). Chemical precipitation is effective, but it produces a large amount of sludge, has slow metal precipitation, requires a large amount of chemicals to reduce metals to an acceptable limit for discharge, and has a high sludge disposal cost (Pohl, 2020). Flotation requires less space, the method is flexible, simple, and the produce low volume sludge. However, it is not efficient due to the high capital, operational and maintenance cost needed (Taseidifar *et al.*, 2017). Coagulation and flocculation produce a lot of sludge, which is ineffective with natural coagulants, selective for specific metals, and thus making it ineffective for removing emerging pollutants (Qasem *et al.*, 2021).

2.6.1 Adsorption

Adsorption is a method of separating fluid phase components by transferring solute to the surface of a solid adsorbent (Barakat, 2011). This method is widely used in the removal of toxic metal ions from effluents because it is inexpensive, produces few wastes, and produces high-quality treated water and is environmentally friendly (A. Hussain *et al.*, 2021). Zeolites and carbon-based adsorbents are the most frequently used adsorbents because of their large surface area, simplicity in chemical modification, excellent adsorption efficiency and porosity. However, they are expensive, difficult to regenerate and non-economical (Duan *et al.*, 2020). The selection of adsorbent to use is heavily influenced by surface area, porosity, cost-effectiveness, and the polarity and distribution of functional groups (Ali *et al.*, 2016). Current research has focused on the use of non-convictional low-cost adsorbents that are inexpensive, readily available, and environmentally friendly for the removal of heavy metals in water like agricultural waste and industrial by-products (Younas *et al.*, 2021). In this study we are going to use agricultural waste as an adsorbent.

2.6.2 Use of Tea Wastes as Adsorbent for Heavy Metal Adsorption

Tea is one of the most popular beverages, with approximately 3.5 million tons consumed globally each year (Younas *et al.*, 2021). Due to improvement in living standards, tea has become an essential drink in our lives. After brewing tea, the spent tea becomes a waste that must be disposed of causing a disposal problem (S. Wan *et al.*, 2014). Tea waste physiochemical properties, such as high surface capacity and fast adsorption kinetics, make it an ideal low-cost adsorbent for the removal of metals from water, as well as an inexpensive precursor material for the production of activated carbon (Hussain *et al.*, 2018). Because tea leaves contain functional groups, a third of the total dry matter should have good potential as a metal scavenger from water. The functional groups in lignin, tannin, or other phenolic compounds that are responsible for contamination are primarily carboxylate, aromatic carboxylate, phenolic hydroxyl, and oxyl groups (Nandal *et al.*, 2014). Tea leaves' insoluble cell walls contain cellulose, hemicellulose, lignin, and condensed tannins (Thapak *et al.*, 2015). Dwivedi and Rajput (2014), studied use of tea waste in removal of copper and cadmium. Copper ion is adsorbed 89% with 120 minutes contact time while cadmium ion is adsorbed 87% with 120 minutes contact time. The active carbon of tea waste

produced by use of hydro char of tea waste obtained from tea factories can be used as adsorbent in removal of heavy metals. In this study we are going to use hydrochar of tea waste in removal of heavy metals from water.

2.7 Removal of Heavy Metals Using Multiwalled Carbon Nanotubes (MWCNTS)

Carbon nanotubes have recently been used in the removal of heavy metals from water where the optimum values of some important parameters such as pH, adsorbent dose and contact time were determined. MWCNTs were modified by Vuković *et al.* (2011), where individual and competitive adsorption characteristics of cadmium and lead ions was studied. The study found that the adsorption of Pb^{2+} and Cd^{2+} on MWCNTs is highly pH dependent, with the maximum adsorption occurring at a pH of 6.2. In a study of Pristine MWCNTs the heavy metals' interaction with the surface of the MWCNTs was demonstrated using an intra-particle diffusion model. The metal ions in the following sequence competed for active binding sites on the MWCNT: Cu (II) Zn (II) Pb (II) Cd (II) (Salam *et al.*, 2012). Li *et al.* (2011), studied the adsorption of lead on the presence of surfactants using oxidized MWCNTs. In this study when the concentration of the sodium dodecyl benzene surfactant (SDBS) was increased to 2mmol/L, it increased lead adsorption on MWCNTs from 17 to 80%. Increase in the concentration of SDBS to 4 mmol/L, makes removal of Pb reduced to 45%. The addition of octyl-phenolethoxylate (TX-100) increased lead removal by 4%.

2.7.1 Regeneration of Adsorbent

Desorption is commonly used to restore the adsorbent for future use, and metals can be recovered by extraction from the liquid phase, preserving the naturally low-cost adsorbents (Bayuo *et al.*, 2020). Proton exchange with acids, chelating agents, or exchange with other ions can be used to perform desorption. The type of adsorbent used and the metals adsorbed influence the choice of desorbing agents (Mishra, 2014). Regeneration of adsorbent leads to recovery of adsorbent molecules, reduces secondary waste and cost of adsorption and help in understanding the adsorption process (Mudhafar *et al.*, 2020). The efficiency of bio adsorbent for heavy metal removal depends on the regeneration of bio adsorbent after metal desorption (Sireesha *et al.*, 2022). There will be secondary pollution from the used adsorbents and the chemicals used to treat the adsorbents for metal recovery in both cases. The disposal of

used adsorbents containing heavy metals may be done after recovery of contaminants or directly without heavy metal recovery (Tzou *et al.*, 2007). Different regenerating agents, including acids, alkalis, and chelating agents (like ethylene diamine tetra acetic acid), can be used to regenerate and reuse adsorbents (Vakili *et al.*, 2019). For the desorption of heavy metals from chemical or chemically altered adsorbents, alkalis are effective desorbing agents; acids are effective for the desorption of bio- adsorbents; and chelating agent EDTA is the most effective desorbing agent for the desorption of biomass. Many of the adsorbents can be effectively recycled after regeneration (Lata *et al.*, 2015).

2.8 Theoretical Framework

2.8.1 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is a potent and sensitive technique for analyzing any varying signal to its constituent frequency components in a single operation. Infrared spectroscopy is used to analyze micro samples down to the nanogram level and is used for structure elucidation (Smith, 2011). IR is produced by an aperture that controls the amount of radiation. A single pulse of radiation with a wavelength range of 400-4000 cm^{-1} is applied to the sample, resulting in partial absorption and transmittance. The amount of analyte of interest in the sample is determined by the amount of radiation transmitted or absorbed by the sample, and the resulting beam from the sample is detected and an infrared spectrum is obtained (Qhanavati *et al.*, 2021). A specific molecule can be recognized by the distinctive infrared spectra that various materials produce due to their various vibrations. For instance, N-atom nonlinear molecules display $3N-6$ fundamental vibrations. For a vibration to be IR active it must induce a change in the dipole moments of the vibrating molecule thus symmetric vibrations do not appear in the IR spectrum. The infrared spectrum only shows molecular vibrations that are IR active (Xaplanteris *et al.*, 2015).

2.8.2 X-ray Diffraction (XRD)

X-ray diffraction will be used to obtain structural information of a given crystalline solid. The technique will be used to determine the crystallinity degree of various materials where some polymers are non-crystalline while others are cellulose polymers (El Naeem *et al.*, 2022). An amorphous substance will not refract, whereas any

crystallinity substance, even if blended with an amorphous substance will diffract (Musarurwa & Tavengwa, 2020). XRD peaks are produced by the constructive interference of a monochromatic beam of X-rays dispersed at specific angles from each pair of lattice planes in a sample. The peak intensities are determined by the arrangement of atoms within the lattice. As a result, the X-ray diffraction patterns are the fingerprints of periodic atomic configurations in a specific material (Bilal, 2022).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Study Area

The study was conducted at River Kathita in Meru County. River Kathita has its source in Mt. Kenya around Ithangune and Rutundu hills, it flows in a north-easterly direction, easterly through thick equatorial rainforest towards Meru town and in a south easterly direction through Tharaka Nithi County after which it joins River Tana at Kibuuka waterfalls. It is also northernmost of the Mt Kenya tributaries of River Tana. River Kathita, located between longitudes $037^{\circ}.56990^{\circ}\text{E}$ and $038^{\circ}.00236^{\circ}\text{E}$ and latitudes $00^{\circ}.01329^{\circ}\text{N}$ and $00^{\circ}.26667^{\circ}\text{S}$ is in eastern part of Kenya and has a basin with an altitude ranging from 472 – 1982 meters above sea level (Recha *et al.*, 2017).

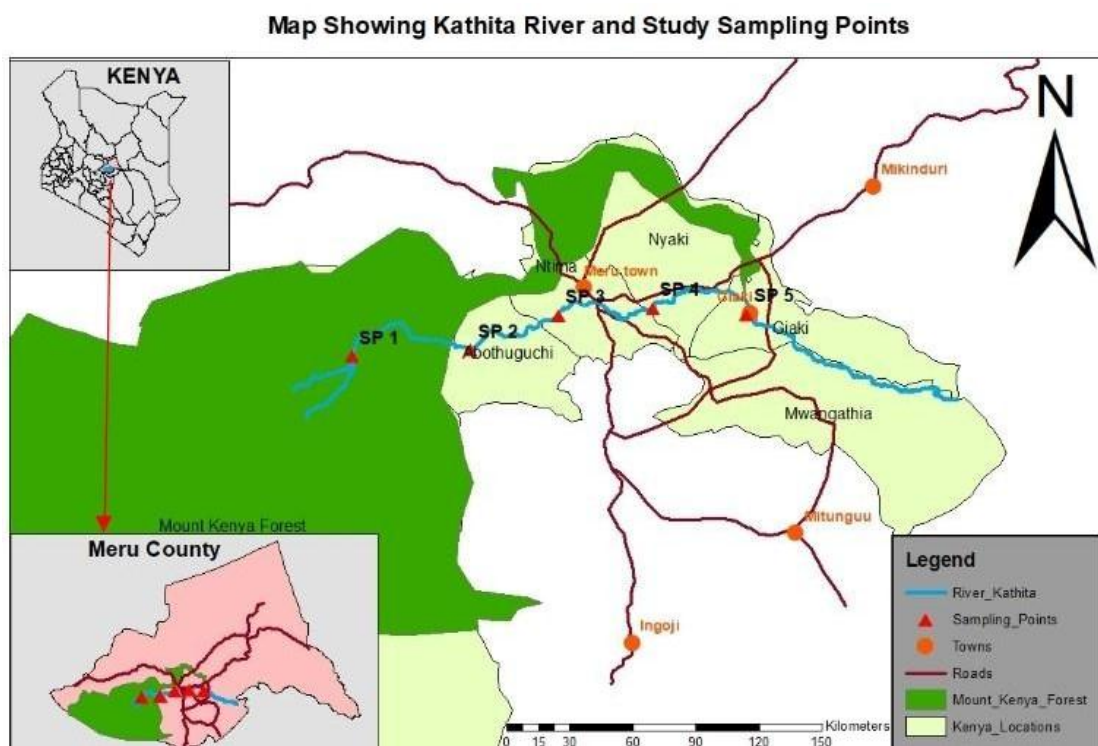


Figure 2: Area Map (Surveys Maps of Kenya).

3.2 Research Design

Experimental research design was used to identify factors that might affect the experimental results, ensure the effect of uncontrolled factors are kept minimum and use of appropriate statistical methods for interpreting the results obtained in order to determine the physicochemical, bacteriological and heavy metal levels of River Kathita. Triplicate samples were collected from 4 sampling points during dry season (February 2024) and wet season (December 2023). The 4 sampling points were

established at varying intervals based on the surrounding activities. The first sampling point was located at Kathiranga after the forest. The second sampling point was located in Nthimbiri where there is mainly tea farming and it is before the town (Meru). The third sampling point was located in Nkabune that is immediately after the town (Meru). This helps access the level of contamination of the water in the town. The last sampling point will be located in Giaki where farming is minimal.

3.3 Sample Size

The sample size was calculated using the formulae proposed by Singh and Masuku (2014),

$$n = t_a^2 S^2 / E^2$$

Where n- desired sample size.

S- standard deviation of observation.

E- permissible in estimate of mean.

t_a – value of a 5 % level of significance

Equation 1: Calculating sample size formula

This entailed carrying out a pilot study from each of the 4 regions in order to determine the mean, standard deviation and the permissible error was assumed to be 0.5 %. This enabled us to determine the total number of samples to be taken in each region (Singh & Masuku, 2014). The estimated number of samples will be a total of 72 samples for both dry and wet seasons.

3.4 Materials

3.4.1 Reagents

Reagents used for the study were; Distilled water, phenolphthalein indicator, HCl 34.5%, H₂SO₄ 95-97%, KOH 90%, (NH₄)₆Mo₇O₂₄.4H₂O 99%, KH₂PO₄ 99%, KBr, Silicon molds, Aluminum stubs, Carbon film. The chemicals were purchased from Loba Chemie.

3.4.2 Apparatus

The apparatus required were; Beaker, Volumetric flask, Ph meter (HACH model), Conductivity meter (HACH-USA), Turbidity meter (HACH model), Dissolved Oxygen meter (HACH model), Whatman 42 Filter paper, Analytical balance, Hotplate, Oven,

UV-Visible spectrophotometer (1800 Shimadzu), Ultrasonic bath, Ultramicrotone, Water glass, plastic bottles for sample collection, Erlenmeyer flask.

3.5 Water Sample Collection

Water samples and sediments were collected randomly in triplicate from four selected sampling points identified in the study area during the dry season (February 2024) and wet season (December 2023). Grab sampling technique was used. The sampling bottles were disinfected with methylated spirit before sample collection, dipped below the water surface ensuring the mouth of the bottle face water current (Yilma *et al.*, 2019). 500ml of water samples was collected. About 250 ml of water sediments below the water were also collected. The samples were stored in cooler containing ice then delivered to Chuka University laboratory and analyses was done between March 2024 and March 2025.

3.6 Water Sample Preparation

3.6.1 Water Temperature

Temperature was also measured using a temperature sensor of pH meter (HACH model). The temperature sensor of the pH meter (HACH model) was immersed in water to a depth of 10cm, allowed to stabilize for some time and temperature read in degree Celsius (Qin *et al.*, 2018).

3.6.2 Water pH

Water pH was determined using a pH meter (HACH model). The pH meter (HACH model) was lowered into the river to a depth of 10cm and allowed to stabilize. The pH was then read directly and recorded (Juneja & Chaudhary, 2013).

3.6.3 Water Turbidity

Water turbidity was measured using a turbidity meter (HACH model). Water samples from different sampling points were collected and taken to Chuka University laboratory where the turbidity was determined (Rice *et al.*, 2012).

3.6.4 Water Electrical Conductivity

Water conductivity was determined using a conductivity meter (HACH-USA). Water

samples from different sampling points was collected and taken to Chuka University laboratory where conductivity was determined (Rice *et al.*, 2012).

3.6.5 Water Total Dissolved Solids

Water samples collected from different sampling points were taken to Chuka University laboratory. The weight of a clean empty beaker was determined using an analytical balance and recorded. 50ml of the water sample from different sampling points was put on the weighed beaker, digested on a hotplate where HNO₃ is used till almost dry and transferred on an oven and dried completely. The beakers were left for some time to cool and then measured. The mass of empty beaker was subtracted from the mass of the beaker and dried solids and the total mass of dissolved solids obtained as shown in equation 3.1 (Rice *et al.*, 2012).

$$\text{Total mass of dissolved solid} - \text{Mass of beaker and dried solids} = \text{Mass of empty beaker}$$

3.6.6 Total Dissolved Oxygen (DO)

Dissolved oxygen was measured using a dissolved oxygen meter (HACH model). Water samples were collected from different sampling points and taken to Chuka University laboratory. The DO meter was immersed in a beaker containing the water sample while stirring the water. The readings were then allowed to stabilize and read in mg/l (Rice *et al.*, 2012).

3.6.7 Phosphates

Water samples collected from different sampling points were taken to Chuka University laboratory. 100ml of the water samples was measured in a beaker, 1ml sulphuric acid added followed by 5 mls of nitric acid. The samples were then digested in a hotplate, 2 drops of phenolphthalein indicator added followed by stepwise addition of potassium hydroxide to control pH. A complex of phosphomolybdovanadate was formed by transferring the solution in a 100ml volumetric flask and topping up to the mark using distilled water, 10 mls of the solution was then transferred into a beaker and 10ml of ammonium molybdate added and allowed to settle for 5 minutes.

4.390g of potassium dihydrogen phosphate was measured and transferred to a 100ml beaker, dissolved with distilled water, and the solution transferred to a 1litre volumetric

flask with distilled water added to the mark. 0.2ppm, 0.4ppm, 0.8ppm and 1ppm phosphate standards were prepared from this stock solution. The standards were used to calibrate the UV-Vis spectrophotometer (Shimadzu UV-1900i), and each sample's concentration determined at a wavelength of 880nm (Adams, 2017).

3.6.8 Nitrates

Water samples were collected from different sampling points and taken to Chuka University laboratory. 100ml of the water samples was measured, 1ml of HCl added and put in a 250 ml beaker. 1.6306 g of KNO₃ weighed, dissolved in a 100ml beaker and transferred into 1000ml volumetric flask. Distilled water was then topped up to the mark and served as nitrate stock solution and 1ppm, 2ppm, 4ppm, 8ppm and 10ppm standards of nitrate prepared from it and 1ml of HCl added to each. The standards were then used to calibrate the UV-Visible spectrophotometer (Shimadzu UV-1900i) and the concentration of nitrates in each sample determined at 220nm (Rice *et al.*, 2012).

3.6.9 Heavy Metals

Water samples and sediment collected were used. A volume of 90 ml of each sample and a blank was measured and put in labelled 100 ml beakers. Ten (10) ml of nitric acid was added to each sample and digested in a hotplate to 10ml. The digested samples were filtered using 0.42µm Whatman filter papers onto 50 ml volumetric flasks and topped up to the 50 ml mark using distilled water. The salt of each metal ion was used to prepare the standards in the range of 5 ppm, 10 ppm and 20 ppm. The levels of Cu, Pb, Cd and Fe were determined using a PG-990 AAS at Chuka University (Rice *et al.*, 2012).

3.6.10 Bacteriological Analysis

The samples were tested for bacteriological quality using a multi-tube fermentation method and broth analysis. Bacteriological testing included presumptive, confirmatory, and final tests. Presumptive test analysis was performed to count total coliforms, while confirmatory test analysis was performed on the samples using brilliant green broth to count fecal coliforms (Skelton, 2013). The Presumptive Coliform Test was used to determine the Most Probable Number (MPN) of Coliform using a multi-tube technique. Positive Presumptive tests were followed by additional tests to confirm the presence of

E. coli. Samples were cultured using EMB agar. Samples were streaked on agar plates, labeled with a source code, and incubated at 37°C for 24-48 hours. The positive samples from the previous 24 hours were cultured again. Positive samples were cultured on Lactose broth and Nutrient agar slant and incubated for 24 hours at 37°.

3.7 Heavy Metals Adsorption

3.7.1 Oxidation of Multiwalled Carbon Nanotubes

MWCNTs were purchased from Hongwu International Group Ltd. Analytical balance was used to weigh 500mg of MWCNTs and they were put in a 250 ml round bottomed flask, and 100 ml of 32% concentrated HCl added to remove impurities. The suspension was stirred for 2 hours, filtered and the MWCNTs washed with distilled water until the solution was neutral. The tubes were dried in vacuum oven at 80°C overnight. The MWCNTs were functionalized using a mixture of 6 M H₂SO₄ and 6 M HNO₃ in a ratio of 1:3 at 80°C for 19 hours and sonicated for 4 hours at 70°C. The mixture was filtered using glass microfilters with a pore size of 0.45 μm, washed till a neutral pH and dried overnight at 80°C. The functionalized tubes were stored in glass vials.

3.7.2 Dispersion of Multiwalled Carbon Nanotubes

Oxidized and raw MWCNTs were dispersed in distilled water for 30 minutes using an ultrasonic bath. After allowing the samples to decant for 24 hours' dispersion of the Multiwalled carbon nanotubes was observed. (Rodríguez *et al.*, 2020).

3.7.3 Tea waste collection

Tea waste was collected from Githongo tea factory, washed and rinsed with distilled water and dried in an oven. After drying it was crushed using a mortar and pestle and kept in a plastic bottle and the bottles preserved in a desiccator before the time of the use to minimize contact with humidity.

3.7.3.1 Surface Functionalization of the Tea Waste

500ml of 0.5M nitric acid was used to treat the powdered tea waste. For 12 hours at a speed of 160rpm, the mixture was shaken. pH was adjusted until neutral by filtering and washing the solution with distilled water (Rashed *et al.*, 2019).

3.7.4 Preparation of Hydro Char of Tea Waste

Analytical balance was used to weigh 20g of the collected tea waste it was added into 160ml distilled water and transferred to high pressure Amar autoclave reactor for synthesis of hydro char tea waste (HTW) (Liu *et al.*, 2019). The hydrothermal treatment was carried out at 180°C for 3 hours.

The autoclave reactor was then cooled to room temperature, the produced HTW filtered, washed several times with distilled water, and dried at 105°C for 12 hours. In order to create active carbon tea waste, 6 g of dried HTW was combined with 12 g of potassium hydroxide, placed in a stainless-steel container, and carbonized at 800°C for 60 minutes with nitrogen flowing through it at a rate of 120 mL/min (Sevilla *et al.*, 2020).

3.7.4.1 Tea Wastes/Multiwalled Carbon Nanotubes Composite

In a mortar, a mixture of modified hydrochar of tea waste, oxidized MWCNTs and a binder was grounded and sieved to a 63-nm particle size. Deionized water was added, and the mixture stirred by an electric stirrer for 24 hours (500rpm). Filtering and drying at 105°C followed a deionized water wash of the mixture (Rodríguez *et al.*, 2020).

3.8 Characterization of the Adsorbents

X-ray diffraction (XRD), Scanning electron microscopy (SEM) and Fourier Transform Infrared (FTIR) (Shimadzu 1S) were used to characterize raw and oxidized MWCNTs dispersed in distilled water (Malik *et al.*, 2015).

3.8.1 Structural Analysis

For each adsorbent, a sample of oxidized MWCNTs, modified hydrochar of tea waste, and tea waste /MWCNTs composite were mixed in a 1:1 ratio with KBr. The pellet was then made using the press pellet technique. An FTIR (Shimadzu 1S) with a frequency range of 4000- 400cm⁻¹ was used to analyze the pellet (Cheng *et al.*, 2011). A XRD analysis of the adsorbent was carried out using Philips® PW 1710 diffractometer at a rate of 20 per min (Omri & Benzina, 2012).

3.8.2 Adsorption Experiments

At room temperature, 1.0g of each adsorbent was added to a solution containing known

amounts of metal ions. Whatman 42 filter paper were used to filter the composite and modified tea waste hydrochar solution after being shaken at 120 rpm and MWCNTs exposed to oxidation at 350 rpm for a predetermined amount of time. ICPMS was used to determine the amount of metal ions in the filtrate (Suliman, 2017). The average value of the metal's concentration was calculated by running three sets of the experiments. Adsorption experiments at doses of 0.5g, 1g, and 2g for each adsorbent were conducted to ascertain the impact of adsorbate dose. Utilizing 1.0M HCl and 1.0M NaOH to adjust the sample's pH, adsorption was assessed at pH values of 2,4, 6, 8 and 10. At 0- 50 minutes of contact time, the adsorption capacity was assessed. Experiments were carried out at various temperatures, including 25°C, 35°C, 40°C, 45°C and 50°C, in order to study the effect of temperature (Rashed *et al.*, 2019). The adsorption capacity was determined using the following equation.

$$q_e = \frac{(C_0 - C_e)V}{m}$$

Where: q_e - Adsorption capacity

C_0 – Initial concentration of the metal in aqueous solution in mg/L

C_e – Equilibrium concentration of metal in aqueous solution in mg/L

m – Mass of the sorbent

V – Total volume of the solution

Equation 3: Calculation of adsorption capacity equation

3.8.3 Desorption and Regeneration of Adsorbent

For desorption experiment, previously adsorbed metal ions on tea waste were transferred into a flask containing 100ml of desorbing agents. Five different desorption agents: de-ionized water, tap water, 0.1M NaOH, 0.1M HCl and 0.1M H₂SO₄ were used to desorb the metal ions from adsorbent. 40 ml desorption agent were kept in 100ml Erlenmeyer flask mixed with adsorbed metal ions, agitated for 60 minutes with continuous agitation at a 120 rpm and 30⁰ C. After equilibration the mixture was filtered using Whatman 42 filter paper. The concentration of the metal ions in the filtrate was determined using UV-Vis spectrophotometer (1800 Shimadzu) (Kwon & Jeon, 2012). Percentage desorption was calculated using the following equation (Katsou *et al.*, 2011).

$$\text{Desorption efficiency (\%)} = C_{de}/C_{ad} \times 100$$

Where;

C_{de} - the amount of metal ions adsorbed.

C_{ad} - the concentration of metal ions desorbed.

Equation 4: Calculation of desorption percentage

The recovered adsorbent was dried at 105⁰C to a constant mass and the regenerated adsorbent used in adsorption-desorption cycles to determine the reusability of the hydrochar of tea waste. Mass of adsorbent at equilibrium was calculated using the equation below (Katsou *et al.*, 2011).

$$Qd = C_{de}/m \times V$$

Where; C_{de} - the amount of metal ions adsorbed in mg.

m - the mass of adsorbent

V - the volume of desorbing solution in L

Equation 5: calculation of mass of adsorbent at equilibrium

3.9 Optimization of Parameters in Adsorption Process

Batch experiments were carried out to determine the adsorption isotherms and kinetics of heavy metals onto the adsorbent in 250 ml glass flasks at 120 rpm. Experiments were carried out in triplicates and average values used for further computation. A control experiment was performed for each experiment to confirm whether any heavy metal is adsorbed on the glass container. This was accomplished by measuring 50 mL of each heavy metal standard solution at 5 mg/L in a 250 mL conical flask without the adsorbent. It was measured at different time intervals while shaking at 120 rpm to confirm if any solute was lost to the glass container. This process was repeated for all of the other variables.

3.9.1 Effect of Contact Time

The adsorption kinetic experiments were performed by batch technique separately and in triplicate. A mass of 0.1 g of the adsorbent was dispersed into 250 ml conical glass flask containing 50 ml of a 5 mg L⁻¹ heavy metal solution and agitated at 120 rpm using an overhead temperature-controlled shaker. The kinetic data was then be fitted to two kinetic models, namely; pseudo-first-order and pseudo-second-order (Revellame *et al.*, 2020), represented in the equations below:

$$\text{Pseudo-first-order model: } \text{Log}(q_e - q_t) = \text{Log } q_e - \frac{k}{2.303} t \dots\dots$$

$$\text{Pseudo-second-order model: } \frac{t}{q_t} = \frac{1}{k_2(q_e)^2} + \frac{t}{q_e} \dots\dots\dots$$

Where q_e - Equilibrium adsorption capacity

K , K_2 and K_p - Rate constants

t (mins) and q_t (mg g^{-1}) - Time and amount adsorbed at equilibrium time respectively

Equation 6: Calculation of kinetic models

The slope gave the rate constant in the pseudo-first-order model, while the intercept gave the rate constant in the pseudo-second-order model.

3.9.2 Effect of pH

The effect of pH on heavy metal removal was analyzed over a pH range of 2 to 10. 50 ml of each heavy metal solution and 0.1 g of adsorbent placed in stopper glass conical flask and pH adjusted using 1 M HCl and 1 M NaOH solutions. The solution was then agitated at 120 rpm at room temperature until equilibration.

3.10 Interference Studies

All of the heavy metal stock solutions (100ppm) were prepared and diluted to lower concentrations of 5ppm, 10ppm, and 20ppm of each metal solution. Metal ion concentration was studied by slowly adding 5ppm of another metal ion solution to a volumetric flask (example Pb), and the effect on the adsorption of the initial metal studied. The procedure was repeated with various metal ion concentrations, pH adjusted, and temperature adjusted while studying the impact on adsorption (Nekouei & Nekouei, 2014).

3.11 Data Analysis and Presentation

Data was analyzed using two-way analysis of variance to ascertain how various variables differ in relation to sampling points and season. Less significant differences (LSD) at $\alpha=0.05$ was used to separate significant means. The collected data was analyzed using two-way ANOVA to ascertain the efficacy of the adsorbents. The mean values obtained were compared with NEMA standards for domestic purpose in order to ascertain whether the remediated water can be used for domestic use.

3.12 Ethical Considerations

The proposal was presented to the Chuka University Ethics Committee for approval, and a research permit from NACOSTI requested and obtained. Materials and methodologies to be used were reported with a lot of honesty. Carelessness, plagiarism and biasness was avoided. In cases where particular information was obtained from other people's work, it was acknowledged and only new information was published for purpose of dissemination of information and for future research. The appropriate citations were used in this study. Laws and regulations governing environmental pollution, handling and disposal of toxic materials were followed strictly to avoid health hazard.

CHAPTER FOUR
RESULTS AND DISCUSSION

4.1 Physical and Chemical Parameters

4.1.1 Physiochemical Parameters During Wet and Dry Seasons

Table 1: Physiochemical parameters of river Kathita during dry season

Location	Cond ¹	Turb ²	pH	DO ³	Temp ⁴	NO ₃ ⁵	P0 ₄ ⁶	TDS ⁸
1	104.467 ^f	2.120 ^c	7.325 ^a	4.583 ^a	24.033	0.136 ^k	0.036 ^{bc}	139.33 ^{ab}
2	100.300 ^{fg}	3.780 ^{bc}	7.193 ^a	4.133 ^b	24.200	0.143 ^m	0.032 ^g	85.00 ^d
3	160.333 ^b	9.398 ^a	6.560 ^b	4.137 ^b	24.266	0.173 ^j	0.037 ^b	105.33 ^{bcd}
4	172.800 ^a	9.267 ^a	6.394 ^c	4.773 ^a	24.200	0.216 ⁱ	0.025 ^g	119.33 ^{ac}
5	91.432 ^h	5.533 ^b	7.288 ^a	4.743 ^a	24.267	0.286 ^d	0.033 ^{ef}	113.00 ^{abcd}
6	98.306 ^g	6.173 ^b	7.213 ^a	4.890 ^a	24.267	0.279 ^g	0.036 ^{bc}	110.67 ^{abcd}
7	110.357 ^e	4.350 ^{bc}	7.265 ^a	4.053 ^b	24.133	0.294 ^b	0.040 ^a	126.00 ^{ab}
8	122.502 ^d	3.910 ^{bc}	7.281 ^a	4.117 ^b	24.200	0.289 ^c	0.035 ^{cd}	90.67 ^{cd}
9	134.289 ^c	5.700 ^b	7.292 ^a	4.770 ^a	24.086	0.272 ^h	0.040 ^a	113.33 ^{abcd}
10	133.503 ^c	4.563 ^{bc}	7.318 ^a	4.669 ^a	24.267	0.299 ^a	0.037 ^b	116.67 ^{abcd}
11	126.801 ^d	4.717 ^{bc}	7.284 ^a	4.783 ^a	24.200	0.285 ^e	0.034 ^{de}	128.33 ^{ab}
12	125.156 ^d	4.746 ^{bc}	7.293 ^a	4.113 ^b	24.300	0.283 ^f	0.035 ^{cd}	100.00 ^{bcd}
Means	123.353	5.354	7.142	4.511	24.213	0.246	0.035	112.306
CV (%)	2.351	28.931	1.231	3.359	0.511	0.068	2.428	17.005
LSD ($\alpha=0.05$)	4.886	2.881	0.148	0.255	0.208	0.0003	0.005	32.183

¹ Conductivity, ² Turbidity, ³ Dissolve oxygen, ⁴ Temperature, ⁵ Nitrate, ⁶ Phosphates, ⁷ Total suspended solids, ⁸ Total dissolved solids

Table 2: Physiochemical parameters of river Kathita during the wet season

Location	Cond ¹	Turb ²	pH	DO ³	Temp ⁴	NO ₃ ⁵	PO ₄ ⁶	TDS ⁸
1	84.167 ^{fgh}	3.27 ^d	7.429	9.820 ^b	24.066 ^{abc}	0.164 ^m	0.066 ^g	143.333 ^c
2	82.733 ^{gh}	5.856 ^{bcd}	7.499	10.093 ^a	23.600 ^d	0.174 ^l	0.071 ^{de}	163.333 ^{cd}
3	117.100 ^b	7.823 ^b	7.439	10.123 ^a	23.600 ^d	0.179 ^k	0.074 ^{bc}	176.667 ^{bc}
4	145.367 ^a	14.837 ^a	7.434	9.846 ^b	24.233 ^a	0.273 ^j	0.073 ^{bc}	193.333 ^{ab}
5	90.670 ^{cde}	3.27 ^d	7.426	9.830 ^b	23.700 ^b	0.440 ⁱ	0.069 ^e	178.333 ^{bc}
6	87.513 ^{defg}	14.837 ^a	7.433	9.840 ^b	23.900 ^{bc}	0.477 ^h	0.072 ^{cd}	215.000 ^a
7	84.903 ^{efgh}	7.306 ^{bc}	7.433	10.163 ^a	24.133 ^a	0.480 ^g	0.075 ^b	192.333 ^a
8	82.600 ^{gh}	4.61 ^{cd}	7.496	10.143 ^a	23.700 ^b	0.483 ^f	0.075 ^b	183.667 ^{bc}
9	92.520 ^{cd}	3.27 ^d	7.426	9.830 ^b	23.700 ^b	0.486 ^d	0.069 ^{ef}	193.333 ^{ab}
10	94.620 ^c	14.837 ^a	7.433	9.833 ^b	23.900 ^{bc}	0.489 ^c	0.081 ^a	202.333 ^{ab}
11	89.553 ^{cdef}	7.306 ^{bc}	7.433	10.156 ^a	24.133 ^a	0.492 ^b	0.067 ^{fg}	199.333 ^{ab}
12	79.213 ^h	4.61 ^{cd}	7.496	10.106 ^a	23.700 ^b	0.495 ^a	0.074 ^b	189.333 ^{abc}
Means	94.247	7.654	7.448	9.982	23.864	0.386	0.073	185.861
CV (%)	4.035	21.286	0.722	0.918	0.532	0.228	1.857	8.841
LSD ($\alpha=0.05$)	6.409	2.745	0.091	0.154	0.214	0.0015	0.002	27.689

¹ Conductivity, ² Turbidity, ³ Dissolve oxygen, ⁴ Temperature, ⁵ Nitrate, ⁶ Phosphates, ⁷ Total suspended solids, ⁸ Total dissolved solids

The temperature was high during the dry season with a mean value of 24. 213. During the dry season, temperatures varied from 24.03°C to 24.30°C with the lowest mean temperature of 24.03°C recorded at Sp1 and the highest mean temperature of 24.30 °C at Sp12. (Table 4.1). There is a significant difference in temperature among the sampling points. During the wet season, temperature varied from 23.60°C to 24.20°C with the lowest men temperature of 23.60°C recorded at Sp2 and the highest mean temperature of 24.70°C recorded at Sp12 (Table 4.2). There is a significant difference in temperature among the sampling points ($p < 0.05$).

The water pH was seen to be high in wet season with a mean value of 7.448. During the dry season the mean water pH varied from 6.394 to 7.325 with the lowest pH of 6.394 recorded at Sp4 and the highest mean water pH of 7.325 recorded at Sp1 (Table 4.1). There was a slight significant difference in water pH among the sampling points. During the wet season the mean water pH varied from 7.426 to 7.499 with the lowest pH of 7.426 recorded at Sp9 and the highest mean water pH of 7.499 recorded at Sp2 (Table 4.2). There was a no significant difference in water pH among the sampling points ($p > 0.05$).

Water turbidity was seen to be high in wet season with a mean value of 7.654. During the dry season the water turbidity mean varied from 2.120 to 9.398 with the lowest turbidity of 2.120 recorded at Sp1 and the highest turbidity of 9.398 recorded at Sp3 (Table 4.1). There was a significant difference in water turbidity among the sampling points. During the wet season water turbidity mean varied from 3.270 to 14.837 with the mean lowest turbidity of 3.270 recorded at 3 different sampling points (Sp1, Sp5, Sp9) and the highest mean turbidity of 14.837 recorded at 3 different sampling points (Sp4, Sp6, Sp10) (Table 4.2). Rainfall runoff was responsible for this, as it erodes soil from dirt roads, farms, plant debris, animal feces, fertilizers, and other organic and inorganic pollutants that end up in the water systems (Al Sawaf *et al.*, 2024). There was a significant difference in water turbidity among the sampling points ($p < 0.05$). Turbidity in water is caused by suspended matter, including clay, silt, fine organic and inorganic matter, soluble colored organic compounds, plankton, and other microscopic organisms. Turbidity in water samples may vary depending on the size, shape, color, and refractive index of particulates at each sampling point (Ombaka *et al.*, 2012).

Water electrical conductivity was high in the dry season with a mean value of 123.353. During the dry season the mean water electrical conductivity varied from 91.432 to 172.800 with the lowest mean of 91.432 recorded at Sp5 and the highest mean of 123.353 recorded at Sp4 (Table 4.1). There was a significant difference in water electrical conductivity among the sampling points ($p < 0.05$). During the wet season the mean water electrical conductivity varied from 79.213 to 145.4 with the lowest mean of 79.213 recorded at Sp12 and the highest mean of 145.367 recorded at Sp4 (Table 4.2). There was a slight significant difference in water electrical conductivity among

the sampling points ($p < 0.05$).

Total dissolved solids were found to have high mean in wet season with a mean value of 185.861. During the dry season the mean total dissolved solids varied from 85.0 to 139.33 with the lowest mean of 85.000 recorded at Sp2 and the highest mean value of 139.33 recorded at Sp1 (Table 4.1). There was no significant different in the mean of total dissolved solids among the sampling points ($p > 0.05$). During the wet season the mean total dissolved solids varied from 143.33 to 215.00 with the lowest mean of 143.33 recorded at Sp1 and the highest mean value of 215.00 recorded at Sp6 (Table 4.2). There was significant different in the mean of total dissolved solids among the sampling points ($p > 0.05$).

Dissolved oxygen was found to be high during the wet season with a mean of 9.982. During the dry season the mean total dissolved oxygen varied from 4.053 to 4.890 with the lowest mean of 4.053 recorded at Sp7 and the highest mean value of 4.890 recorded at Sp6 (Table 4.1). There was significant different in the mean of dissolved oxygen among the sampling points ($p < 0.05$). During the wet season the mean total dissolved oxygen varied from 9.820 to 10.163 with the lowest mean of 9.820 recorded at Sp1 and the highest mean value of 10.163 recorded at Sp7 (Table 4.2). There was significant different in the mean of dissolved oxygen among the sampling points ($p < 0.05$).

The phosphates were high during the wet season with a mean value of 0.073. During the dry season the mean phosphates level varied from 0.025 to 0.040 with the lowest mean of 0.025 recorded at Sp4 and the highest mean value of 0.040 recorded at two different points (Sp7, Sp9) (Table 4.1). There was a slight significant different in the mean of phosphates among the sampling points ($p < 0.05$). During the wet season the mean phosphates varied from 0.066 to 0.081 with the lowest mean of 0.066 recorded at Sp1 and the highest mean value of 0.081 recorded at Sp10 (Table 4.2). There was a slight significant different in the mean of phosphates among the sampling point ($p < 0.05$). High rates of organic matter decomposition in runoff and interactions between water and sediments from dead plants and animal remains at river bottoms can result in high phosphate levels (Adesuyi *et al.*, 2016).

The nitrates were high during the wet season with a mean value of 0.386. During the dry season the nitrates levels varied from 0.136 to 0.299 with the lowest mean of 0.136 recorded at Sp1 and the highest mean value of 0.299 recorded at Sp10 (Table 4.1). There was a slight significant difference in the mean of nitrates among the sampling points. During the wet season nitrates level varied from 0.164 to 0.495 with the lowest mean of 0.164 recorded at Sp1 and the highest 0.495 recorded at Sp12 (Table 4.2). There was slight significant difference in the mean of total dissolved solids among the sampling points. Increased nitrate concentrations are linked to a number of factors, including storm water, runoff from residential areas, infiltration from landfills, runoff from industrial and agricultural areas, and wastewater discharge into water bodies (Khounda *et al.*, 2012).

4.1.2 Comparison of Physicochemical Parameters During wet and Dry Season with other Studies

The earth's surface warming or cooling during high recharge times when it rains, or the introduction of cold water from the surface, could be the cause of the high temperature during the dry season relative to the wet season (Ombaka *et al.*, 2013). In the upper regions of the Kathita River (SP1 and SP2), the low temperature is primarily caused by the proximity to Mount Kenya, where the melted ice produces cold water. The clearing of vegetation and agricultural activity as you approach the town cause the temperature to rise. However, the release of heat effluent from Meru town has resulted in extremely high temperatures in the areas beyond the town (SP12) (Achieng *et al.*, 2021). High temperatures reduce the solubility of gases such as carbon dioxide and other volatiles, which affect the taste of water (Singh *et al.*, 2014).

According to research by Bonareri (2013), on River Rupingazi cloud cover fluctuation was attributed to temperature variations. During the dry season, there was less cloud cover, which increased indirect solar radiation, leading to higher water temperatures. During the wet season, increased cloud cover reduces direct solar radiation, resulting in lower temperatures. Encroachment of agricultural lands has led to a decrease in riparian vegetation cover, resulting in reduced canopy cover in the study area and contributing to temperature variations.

During the wet season, higher pH levels may result from waste discharges and microbial decomposition of organic matter. Because there is more organic matter in the water during the wet season, an increase in rainfall lowers the pH level. This is a result of the fact that a large number of sampling locations are surrounded by agricultural activity, and the majority of farmers fertilize their fields. As a result, during the wet season, nitrate levels rise and water bodies become more enriched, changing the pH of the water. When too many nutrients are washed into the waterways during rainy seasons, surface runoff in the sampling points surrounding the town lowers the pH of the water, increasing the imbalance of hydrogen ions in the water (Githinji, 2019).

During the dry season, water in certain areas may have a weakly acidic pH due to dissolved carbon dioxide and organic acids from decayed matter leaching into the groundwater (Bhat *et al.*, 2018). Lower pH indicates slightly acidic water, which can cause eye irritation and corrosion in metal pipes used in water distribution systems. Higher pH water can cause gastrointestinal disorders, such as hyperacidity and ulcers, and can also contribute to scale formation in heating systems (Buridi & Gedala, 2014). Pollutants such as chemicals, minerals, and soil/bedrock composition can disrupt the pH balance of a water supply. Chemicals found in the river's soil or bedrock, such as carbonate, bicarbonate, or hydroxide, can dissolve and change the pH of water (P. Li & Wu, 2019) .

According to a study by Mbura (2018), higher pH levels during the wet season can be attributed to waste discharges and microbial decomposition of organic matter. During the dry season, water in certain areas may have a weakly acidic pH due to dissolved carbon dioxide and organic acids from decayed matter leaching into the groundwater. Reduced water volume during the dry season may lead to a decrease in pH levels. When compared to the dry season, the turbidity level was higher during the wet season. Because of soil erosion from farmlands on the upstream slopes, there may be dissolved and suspended particles in the water during the wet season, as indicated by the high levels of turbidity. High levels of turbidity create an environment that is conducive to microorganism survival, which helps to explain why total and fecal coliform counts are higher during the rainy season (Githinji, 2019).

Temperature has a significant impact on the electrical conductivity of river water. Elevated temperature causes a greater amount of dissociated ions, which in turn leads to an increase in electric charge concentration and an increase in conductivity. This explains why the temperature and electrical conductivity were both higher during the dry season. Reduced river water volume may have caused a concentration effect, which could account for the higher dry season conductivity value (Ibrahim *et al.*, 2009). During the two seasons the levels of TDS increased down from sampling point one. This was attributed by human activities like encroachment of riparian land for agriculture, runoff from sewage waste making water get rich in ions that increases the TDS values (Bonareri, 2013). TDS affects water quality parameters such as hardness. For example, high total dissolved solid content may indicate the presence of carbonates. High levels of dissolved solids in drinking water can also increase the risk of cancer and heart disease (Yashoda *et al.*, 2014).

The levels of dissolved oxygen were high during the wet season mainly because during the rainy season dissolved oxygen concentration is often higher because the rain interacts with oxygen in the air as it falls. Oxygen depletion is dependent on the overall quantity and kind of organic material load in the rivers as well as the quantity and kind of bacteria that break down waste that is dumped into them (Speight, 2020). The release of wastewater from residential areas, municipal sewage, and decaying plant matter into receiving water bodies can also lower the concentration of dissolved oxygen due to the increased microbial activity that arises from the breakdown of organic matter (Owhonka *et al.*, 2021). High phosphate levels were observed in this study, during the wet season as a result of run-off, surface catchment, and interactions between water and sediments from dead plants and animal remains at the riverbed in the areas before the town in SP³ and SP⁶. The increased average phosphate concentration in the regions of the town in SP⁹ SP¹⁰ is attributed to the river's slow and shallow water, as well as the overflow of residential area and municipal sewage discharge. Agricultural areas use phosphorus-based fertilizers like ammonium phosphate, resulting in higher phosphate levels during the wet season in sampling points before town. Domestic waste, raw sewage into the river, phosphorus leaching, and surface runoff carrying phosphate-rich fertilizers and manure all contribute to high values during wet season in sampling points after the town (Thriodore, 2004). The low concentration of phosphate in the area may

be attributed to its geology and minimal interference from human activities. Elevated phosphates can lead to digestive issues in humans, and in water, they encourage the growth of weeds and algae that consume a lot of oxygen. The water is contaminated by the toxins produced and stored by these algae (Cotruvo, 2017).

In this study, high nitrate values during the wet season were attributed to both point source pollution at the point where waste water from sewage and car washes around the town was discharged into the river primarily in areas after the town in SP9, SP10 and SP11 and non-point source pollution, which includes runoff from fertilized farms adjacent to the river, manure from livestock and other animal wastes used as organic manure in farms in sampling points before the town where farming is taking place in SP4 and SP6. Increased nitrate levels in the water can lead to stomach cancer in adults and methemoglobinemia, commonly known as "blue baby syndrome," in infants. They can also promote the growth of algae, which contributes to eutrophication (Shuval & Gruener, 2013).

4.1.3 Heavy Metals and Sediments in River Kathita during Wet and Dry Seasons

The levels of Lead (Pb) in samples varied both from the surface water and from the sediment. In sediment samples, Pb values ranged from 0.0364 mg/L to 0.0876 mg/L while in water samples Pb values ranged from 0.0371 mg/L to 0.0771 mg/L during the dry season. The LSD test with Bonferroni adjustment indicated that these differences in levels were statistically significant ($F(4, 45) = 21.34$, $p\text{-value} < 0.001$). Similarly, in sediments samples, Pb concentrations varied from 0.0015 mg/L to 0.0634 mg/L while in water sample Pb values ranged from 0.0068 mg/L to 0.0709 mg/L during the dry season. The LSD test with Bonferroni adjustment also showed statistically significant differences [$F(4, 55) = 16.72$, $p\text{-value} < 0.001$] Table 4.3].

Seasonal lead (Pb) variation exists in both sediment and surface water samples. The natural binding behavior of heavy metals with particulate matter explains why Pb content in sediments surpasses Pb content in surface water (Kudryavtseva *et al.*, 2024). The fluctuations of lead concentrations in surface water through the rainy and dry seasons can be attributed to runoff and sediment disturbances during the wet season which increases lead transport into water systems (Saad *et al.*, 2025).

Table 3: Levels of lead in sediment and surface water during dry and wet season

Sam ple	Levels of Pb in dry season (mg/L)	Levels of Pb in dry season (mg/L)	Levels of Pb in wet season (mg/L)	Levels of Pb in wet season (mg/L)
	Sediment	Surface water	Sediment	Surface water
1a	0.0364 ^b	0.0430 ^b	0.0015 ^h	0.0679 ^a
1b	0.0854 ^a	0.0398 ^b	0.0028 ^h	0.0675 ^a
1c	0.0657 ^{ab}	0.0371 ^b	0.0149 ^g	0.0709 ^a
2a	0.0518 ^{ab}	0.0606 ^{ab}	0.0237 ^f	0.0597 ^{ab}
2b	0.0629 ^{ab}	0.0537 ^{ab}	0.0096 ^g	0.0068 ^c
2c	0.0587 ^{ab}	0.0528 ^{ab}	0.0436 ^{bc}	0.0217 ^c
3a	0.0876 ^a	0.0768 ^a	0.0634 ^a	0.0126 ^c
3b	0.0705 ^{ab}	0.0604 ^{ab}	0.0230 ^f	0.0119 ^c
3c	0.0867 ^a	0.0636 ^{ab}	0.0287 ^{ef}	0.0180 ^c
4a	0.0723 ^{ab}	0.0771 ^a	0.0371 ^{cd}	0.0283 ^{bc}
4b	0.0705 ^{ab}	0.0709 ^a	0.0455 ^b	0.0257 ^{bc}
4c	0.0662 ^{ab}	0.0733 ^a	0.0287 ^{ef}	0.0177 ^c
Mean (Mg/L)	0.0656	0.0586	0.0272	0.0341
CV	27.14%	22.33%	8.01%	31.94%
LSD ($\alpha=0.05$)	0.0123	0.0105	0.0677	0.0342

^a Means followed with the same letters in column are not statistically different at $\alpha=0.05$

Research performed by Kudryavtseva *et al.* (2024), in the Chernaya River documented equivalent patterns of heavy metal distributions including lead because anthropogenic activities and natural hydrological cycles substantially affected seasonal variations. Sediment lead concentrations were found to be high in a lagoon with excessive human activities across winter and summer months (Saad *et al.*,2025). These results demonstrate human activities play a major role in sediment contamination.

The findings from Liu *et al.* (2024), support this study by showing heavy metal levels in Angqu River sediments reached their highest point during the wet season. The periodic changes in water flow and runoff strengthen the introduction of surrounding area contaminants into water bodies. Kundu *et al.* (2012), observed at the Haor area ecosystems of Bangladesh that both sediment excavation and seasonal inundation affect metal concentrations thus demonstrating that water dynamics in wet seasons actively move heavy metals throughout sediments and surface water. Lead contamination ran continuously throughout all seasons in the Wolf River's surface water and sediment areas according to Lightman and Moyo (2024), which indicates ongoing pollution sources and minimal seasonal water dilution effects. Field observations presented by

Davidkova *et al.* (2024), verify that lead concentrations in surface water rise during wet seasons because of elevated runoff and suspended sediment levels. According to Tan *et al.* (2024), the fluctuations in surface water compositions through wet and dry seasons lead to increased water flow that causes metals from sediments to become mobile. The levels of Copper (Cu) in samples varied both from the surface water and from the sediment. In sediment samples, Cu values ranged from 0.413 mg/L to 1.9693 mg/L while in surface water Cu values ranged from 0.0161 mg/L to 0.1319 mg/L during dry season. The LSD test with Bonferroni adjustment indicated that these differences in levels were statistically significant ($F(4, 45) = 25.98$, $p\text{-value} < 0.001$). Similarly, in sediments Cu concentrations varied from 0.0177 mg/L to 0.7039 mg/L while in surface water Cu values varied from 0.0080 mg/L to 0.7039 mg/L during the wet season. The LSD test with Bonferroni adjustment also showed statistically significant differences ($F(4, 55) = 17.56$, $p\text{-value} < 0.001$). These findings highlight the variability in Cu concentrations, emphasizing the need for ongoing assessment and management of copper levels in both sediment and surface water (Table 4).

Table 4: Levels of copper in sediment and surface water during dry and wet season

Sample	Levels of Copper		Levels of Copper	
	in Dry Season (mg/L)	in dry Season (mg/L)	in wet Season (mg/L)	in Wet Season (mg/L)
	Surface water	Sediment	Surface water	Sediment
1a	0.0731 ^{abcd}	1.2873 ^c	0.0892 ^g	0.0892 ^g
1b	0.0439 ^{bcd}	0.4854 ^{hi}	0.1630 ^{bc}	0.2873 ^e
1c	0.0877 ^{abc}	0.4137 ⁱ	0.2434 ^a	0.2222 ^f
2a	0.0439 ^{bcd}	0.5892 ^g	0.3136 ^{de}	0.3136 ^{de}
2b	0.0804 ^{abcd}	0.5468 ^{gh}	0.1857 ^f	0.1857 ^f
2c	0.1096 ^{ab}	0.5329 ^{gh}	0.4181 ^c	0.3567 ^d
3a	0.1319 ^a	1.5556 ^b	0.5329 ^b	0.7039 ^a
3b	0.0161 ^d	0.7442 ^f	0.0431 ^{ef}	0.4444 ^c
3c	0.0219 ^{cd}	0.9693 ^e	0.0241 ^{fg}	0.3567 ^d
4a	0.0124 ^d	1.1864 ^{cd}	0.7039 ^a	0.7039 ^a
4b	0.0351 ^{cd}	1.9240 ^a	0.0146 ^g	0.0257 ^{bc}
4c	0.0314 ^{cd}	1.1837 ^d	0.0080 ^g	0.0177 ^c
Mean (Mg/L)	0.0573	0.9514	0.0341	0.4098
CV	18.07%	3.14%	29.94%	3.44%
LSD ($\alpha=0.05$)	0.0687	0.8932	0.0444	0.0272

a Means followed with the same letters in column are not statistically different at $\alpha=0.05$

The seasonal variations observed in copper concentrations between sediment and surface water, stems from hydrological and anthropogenic factors. During the dry

season when water flow decreased the sediment accumulation became higher at 0.9514 mg/L because sediments carried more copper through precipitation processes (Dugan *et al.*, 2024). Better mobilization of copper occurs during the wet season as surface water copper levels rise to 0.0341 mg/L due to sediment disturbance and runoff effects (Kudryavtseva *et al.*, 2024). The Majes-Camaná basin experienced seasonal heavy metal behavior in sediment layers which was verified by Obada *et al.* (2025), through their research. The study discovered that copper and other metals were released into surface water during flood season because of higher rates of erosion and water movement which confirms the current findings about elevated copper levels in surface water during the wet season. The Angqu River sediments demonstrated higher general copper concentrations in the wet season according to Liu *et al.* (2024), while this research had lower sediment copper levels during the same period. Dissimilarities in local hydrological variables like water movement and sediment transportation strengths may explain this difference between study results.

Kudryavtseva *et al.* (2024), identified major heavy metal variations including copper during different seasons within urban water systems. This research supported findings about increased copper levels in surface water during wet seasons because authors documented that urban runoff along with industrial discharges were responsible for these elevated concentrations. The research by Ikhsani *et al.* (2024), demonstrated how sediment disturbances during wet seasons caused copper to wash into the water column of the Bay of Bengal. Sediments function as a reliable repository of copper because their seasonal variability (3.14% in dry season and 3.44% in wet season) remains lower than that of surface water (18.07% in dry season and 29.94% in wet season). The binding force between copper and particulate matter usually results in sediment stability patterns (Dugan *et al.*, 2024). The research findings confirm that copper distributions in aquatic systems respond to constant transformation from seasonal river patterns and human-made pollution through agricultural waste and industrial wastewater. The natural process of dry period sedimentation followed by wet season mobilization results in repeating cycles of copper availability throughout aquatic ecosystems therefore generating important ecological as well as environmental repercussions.

The levels of Cadmium (Cd) in samples varied both from the surface water and from the sediment. In sediment samples Cd values ranged from 0.0019 mg/L to 0.0305 mg/L while in water surface Cd values ranged from 0.0015 mg/L to 0.0309 mg/L during the dry season. The LSD test with Bonferroni adjustment indicated that these differences in levels were statistically significant ($F(4, 45) = 51.07$, $p\text{-value} < 0.001$). Similarly, in sediments Cd concentrations varied from 0.0065 mg/L to 0.0377 mg/L while in water surface Cd values ranged from 0.0025 mg/L to 0.0442 mg/L during the wet season. The LSD test also showed statistically significant differences ($F(4, 55) = 20.73$, $p\text{-value} < 0.001$).

Table 5: Levels of cadmium in sediment and surface water during dry and wet season

Sample	Levels of Cd in	Levels of Cd in	Levels of Cd in	Levels of Cd in
	Dry Season (mg/L)	dry Season (mg/L)	wet Season (mg/L)	Wet Season (mg/L)
	Surface water	Sediment	Surface water	Sediment
1a	0.0051 ^f	0.0019 ^f	0.0025 ^f	0.0065 ^d
1b	0.0115 ^{ef}	0.0103 ^{de}	0.0045 ^f	0.0191 ^{cd}
1c	0.0145 ^{de}	0.0286 ^{bc}	0.0077 ^{ef}	0.0286 ^{bc}
2a	0.0165 ^{cde}	0.0025 ^f	0.0090 ^{def}	0.0366 ^b
2b	0.0207 ^{bcd}	0.0129 ^{cd}	0.0180 ^{cde}	0.0377 ^b
2c	0.0200 ^{cde}	0.0292 ^{ab}	0.0213 ^c	0.0284 ^{bc}
3a	0.0217 ^{bcd}	0.0305 ^{bc}	0.0194 ^{cd}	0.0305 ^{bc}
3b	0.0234 ^{abc}	0.0204 ^b	0.0227 ^c	0.0377 ^b
3c	0.0239 ^{abc}	0.0216 ^b	0.0219 ^c	0.0284 ^{bc}
4a	0.0292 ^{ab}	0.0186 ^{bc}	0.0281 ^{bc}	0.0267 ^{bc}
4b	0.0239 ^{abc}	0.0263 ^{ab}	0.0353 ^{ab}	0.0181 ^{cd}
4c	0.0309 ^a	0.0292 ^{ab}	0.0442 ^a	0.0304 ^{bc}
Mean (Mg/L)	0.0201	0.0161	0.0196	0.0274
CV	13.80%	14.34%	18.48%	14.75%
LSD ($\alpha=0.05$)	0.0087	0.0127	0.0114	0.0127

^a Means followed with the same letters in column are not statistically different at $\alpha=0.05$

The patterns of cadmium concentration changes across seasons in both water surface and sediment match previous research which shows environmental activities and anthropogenic factors lead to variations of metals in aquatic environments. Surface water mean Cd concentrations were 0.0201 mg/L during dry season compared to 0.0196 mg/L during wet season but sediment Cd concentrations reached 0.0274 mg/L in wet season and 0.0161 mg/L during dry season. Research findings indicate cadmium moves from sediments into water column periods which corresponds to the wet seasons

possibly because of higher runoff and disturbed sediment during heavy rainfall (Obada *et al.*, 2025).

The Majes-Camaná basin of Peru showed matching seasonal patterns according to Obada *et al.* (2025), when surface sediments revealed cadmium levels related to flooding seasons and periods of low water. The research validates the present findings showing that sediment-bound cadmium increases in surface water during the flood season. Saad *et al.* (2025), demonstrated that lagoons with anthropic influences show major seasonal changes in cadmium content which highlights human activities as exasperating factors for seasonal variations of metals in sediments and surface water bodies.

Kudryavtseva *et al.* (2024), established that water system cadmium concentrations in urban areas change because of seasonal fluctuations along with urban runoff levels. The research showed that water flow elevation in the wet season created atmospheric conditions that allowed more cadmium to leach from sediments into surface water bodies thus matching the increased cadmium measurements recorded in this study during the wet season. Liu *et al.* (2024) discovered that the Angqu River sediments accumulated greater amounts of cadmium during the wet season when water flow and sediment deposition reached maximum levels.

Ikhsani *et al.* (2024), examined how seasonal hydrological operations such as sediment transport and water mass movements determine marine cadmium distribution during their Bay of Bengal research. The authors demonstrated that the combination between seasonal runoff water and sediment suspension raises sediment cadmium amounts based on their research results. The cadmium concentration variability measured using the coefficient of variation method showed moderate levels with surface water during wet season exhibiting the most variable concentrations (18.48%). Surface water cadmium levels are strongly affected by external incidents like runoff and human-made discharges since cadmium particles in sediments tend to remain stable (Kudryavtseva *et al.*, 2024).

4.1.4 Comparison of Lead, Copper and Cadmium in Surface Water in Dry and Wet Season

In surface water samples, there was no significant difference in Cd levels between the dry and wet seasons, $t(57.11) = 0.23$, $p = 0.821$. The Cd concentrations were similar across seasons [(Dry: $M = 0.0201$, $SD = 0.0047$; Wet: $M = 0.0196$, $SD = 0.0051$) Figure 3], with a 95% confidence interval for the difference in means of $(-0.0043, 0.0054)$. However, Cu levels differed significantly between seasons, $t(52.98) = -2.74$, $p = 0.008$. Copper level was higher during the wet season ($M = 0.0982$, $SD = 0.0018$) compared to the dry season [$M = 0.0573$, $SD = 0.0422$) Figure 3]. The 95% confidence interval for the difference in means was $[-0.0709, -0.0110]$.

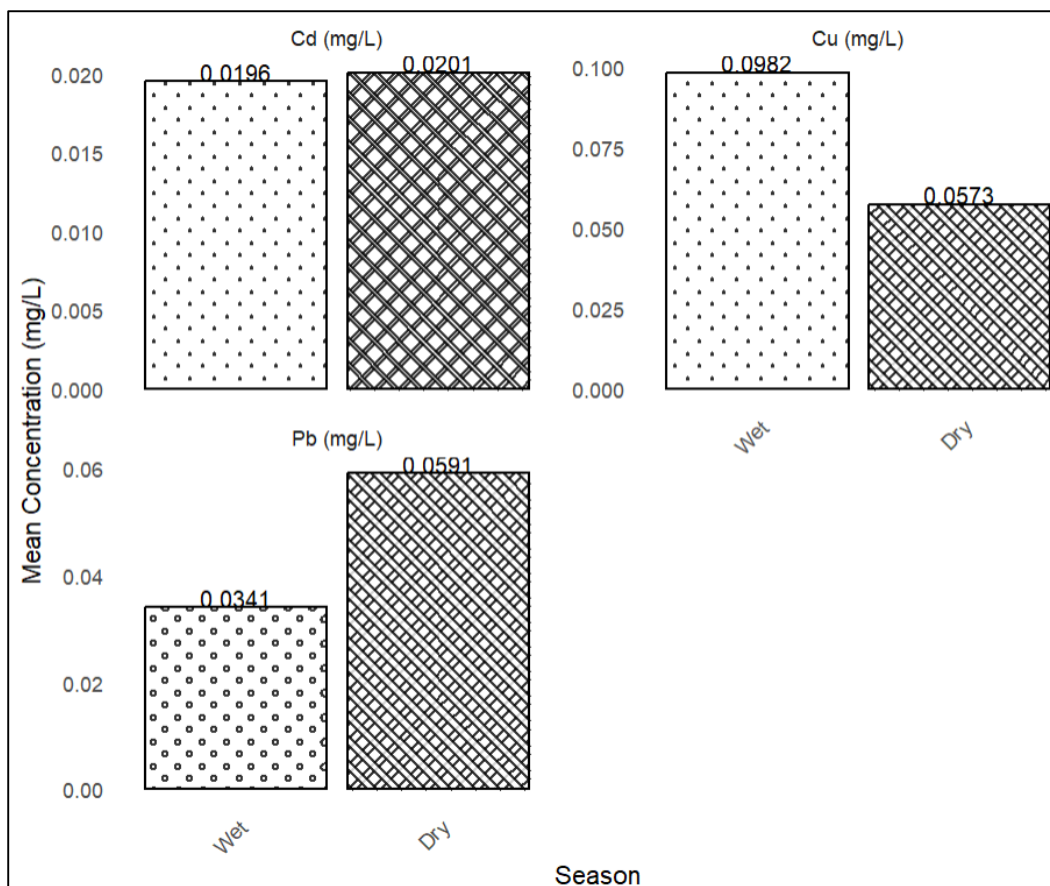


Figure 3: Comparison of lead, copper and cadmium in surface water in dry and wet season

Lead (Pb) levels were also significantly different, with higher concentrations in the dry season ($M = 0.0591$, $SD = 0.0220$) compared to the wet season ($M = 0.0341$, $SD = 0.0150$), $p < .001$. The 95% confidence interval for the difference in means was $[(0.0151, 0.0349)$ Figure 1]. For sediment samples, there was a significant difference in Cadmium (Cd) levels between the dry and wet seasons, $t(66.04) = -4.40$, $p < .001$. Specifically, Cd

levels were higher during the wet season ($M = 0.0274$, $SD = 0.0123$) compared to the dry season ($M = 0.0161$, $SD = 0.0075$). The 95% confidence interval for the difference in means was $(-0.0164, -0.0062)$. Copper (Cu) levels also showed a significant seasonal difference, [$t(47.41)=6.38$, $p<.001$; Figure 3].

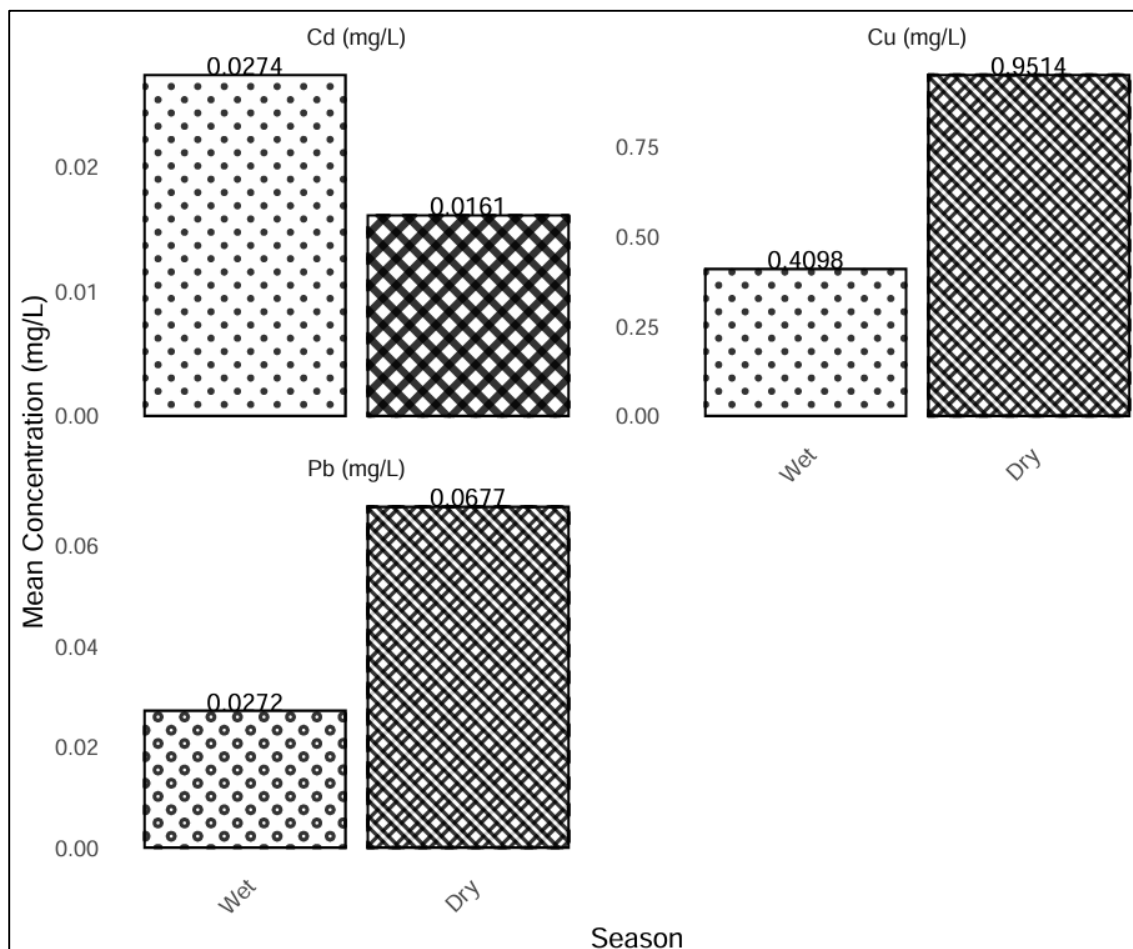


Figure 4: Comparison of lead, copper and cadmium in sediment in dry and wet season

The concentrations of Cu were significantly higher during the dry season ($M = 0.9514$) compared to the wet season ($M = 0.4098$, $SD = 0.1852$). The 95% confidence interval for the difference in means was $[0.3708, 0.7124]$. Lead (Pb) levels were significantly higher in the dry season ($M = 0.0677$, $SD = 0.0203$) than in the wet season ($M = 0.0272$, $SD = 0.0137$), $t(67.89)=10.30$, $p<.001$. The 95% confidence interval for the difference in means was $[(0.0327, 0.0484)$ Figure 4].

The results on Cd levels in Bay of Bengal surface water match those of Ikhsani *et al.* (2024), who discovered minimal seasonal variation due to Cadmiums strong sediment binding ability and its low mobility in water. Liu *et al.* (2024), also detected elevated

metal accumulation in Angqu River sediments during high flow seasons, particularly because of sedimentation processes. The authors supported these results through findings of higher sediment Cd levels in the wet season period. Research results documented by Kudryavtseva *et al.* (2024), demonstrate that copper content in surface water increases during wet seasons because urban drainage and increased erosion rates from rain cause water body contaminant levels to rise. Obada *et al.* (2025), confirmed the relation between lower water flow in dry seasons which enables sediment-driven accumulation of metals leading to reduced metal concentrations in water column.

Surface water lead levels increased during the dry season potentially as a result of lower dilution effects as reported in Saad *et al.* (2025), who studied a contaminated lagoon system. Sediment Pb levels were much higher during the dry season because lead bonds strongly with particulate matter while water flow is minimal according to (Kudryavtseva *et al.*, 2024). The research reveals multiple factors that determine how metals behave in aquatic systems during hydrological season changes. Strategies for effective management need to consider seasonal patterns of metal pollution since they are most at risk during the wet period for Cd and Cu mobilization and during the dry season for Pb accumulation in sediments.

4.2 Bacteriological analysis of River Kathita during Wet and Dry Season

4.2.1 Total Coliforms

The total coliform was found to be as shown in the table below. There was a significant difference in the total coliforms count among the sampling points. The total coliforms were found to be high during the wet season. During the dry season highest total coliform mean was 207.667 cfu/100ml found at Sp10 and the least total coliform mean was 18.667 cfu/100ml found at Sp2. During the wet season highest total coliform mean was 1130.00 cfu/100ml found at Sp10 and the least total coliform mean was 18.333 cfu/100ml found at Sp2 (Table 4.6).

Table 6: Total coliforms during wet and dry seasons

Analysis of total coliform cfu/100ml					
Location	N Obs	Dry season		Wet season	
		Mean	Median	Mean	Median
2	3	18.667	18.000	18.333	18.000
3	3	31.333	35.000	344.000	500.000
4	3	42.333	42.000	530.000	530.000
5	3	55.000	42.000	282.667	50.000
6	3	107.667	108.000	830.000	830.000
7	3	113.333	135.000	630.667	900.000
8	3	77.333	77.000	102.000	102.000
9	3	116.667	87.000	430.667	122.000
10	3	207.667	208.000	1130.000	1130.000
11	3	191.667	230.000	854.667	1200.000
12	3	122.667	123.000	174.000	174.000
Kruskal-Wallis test	$H(11) = 31.718$		$H(11) = 21.812$		
	$p = 0.0008$		$p = 0.0259$		

Surface water obtains higher microbial contamination levels during the wet season because heavy rainfall results in the removal of fecal impurities and agricultural and urban pollutants (Dehghani Ahmadabadi *et al.*, 2024). According to (Chukwu Okeah *et al.*, 2025) studies in the Sombreiro River of Nigeria total coliform counts dramatically rose due to intensified surface runoff together with riverbank erosion during the wet season. A spike in Cabo Frio shallow coastal aquifer coliform levels during wet season conditions was documented by Sabino *et al.* (2024), within Brazilian territory. This research showed that stormwater flow combined with inadequate sanitation systems degrades water quality when rain occurs in the region. According to dos Santos *et al.* (2025), coliform levels in the Dois de Abril stream basin rose significantly during rainy periods because strong surface runoff and increased water flow caused intensified microbial contamination.

The Pasig–Marikina–San Juan River system undergoes changes in microbial contamination levels according to Mamawal and Rivera (2025), who discovered that wet seasons create additional hazards for public health through elevated total coliform measurements. Seasonal changes produced significant differences in total coliform

counts at various sampling sites according to the results from the Kruskal-Wallis test as per the current study.

4.2.2 Faecal coliform

The faecal coliform was found to be as shown in the table below. There was a significant difference in the mean of faecal coliform count among the sampling points. The faecal coliforms count was found to be high during the wet season. During the dry season highest faecal coliforms count mean was Sp10 cfu/100ml found at S10 and the least total coliform mean was 5.333 cfu/100ml found at Sp2. During the wet season highest total coliform mean was 86.00 cfu/100ml found at Sp10 and the least total coliform mean was 11.333 cfu/100ml found at Sp1 (Table 4.7)

Table 7: Total faecal coliforms during wet and dry season.

Analysis of faecal coliform cfu/100ml					
Location	N Obs	Dry season		Wet season	
		Mean	Median	Mean	Median
1	3	5.667	5.000	11.333	12.000
2	3	5.333	5.000	11.667	12.000
3	3	12.333	15.000	30.333	38.000
4	3	17.000	17.000	41.000	41.000
5	3	14.667	8.000	34.000	22.000
6	3	27.333	27.000	66.000	66.000
7	3	22.667	28.000	59.333	73.000
8	3	13.333	13.000	34.000	34.000
9	3	18.333	13.000	46.000	33.000
10	3	32.333	32.000	86.000	86.000
11	3	25.667	31.000	68.333	83.000
12	3	15.333	15.000	38.000	38.000
Kruskal-Wallis test		$H(11) = 25.1723$		$H(11) = 26.4571$	
		$p = 0.0086$		$p = 0.0025$	

Research findings demonstrate that fecal coliform counts rise during the wet season similarly to what this study observed. During the wet season surface water develops high fecal coliform counts because heavy rainfall produces two main sources of contamination: the removal of waste through sediments and agricultural runoff and the

pollution from urban areas (Vivian *et al.*, 2024). Some areas with defective wastewater management systems together with weak sanitation infrastructure demonstrate this regular phenomenon. Research conducted by Fouad *et al.* (2024), in the Fayoum depression, Egypt uncovered that fecal coliform concentrations rose during the wet season caused by increased water flow from agricultural land and areas near residential zones. Atud *et al.* (2025), reported through their research that peri-urban groundwater sources in Cameroon experienced increased microbial levels from fecal coliform counts because of seasonal changes during rainy periods.

The research conducted by Chukwu Okeah *et al.* (2025), determined that Sombreiro River in Nigeria displayed elevated fecal coliform numbers during the seasonal rainfall period. The authors linked these elevations in counts to destructive erosion together with unfiltered sewage and animal waste that entered the river downstream. The results of this study align with the findings because the Kruskal-Wallis test revealed important differences in fecal coliform values between sampling sites which showed seasonal impacts. These research studies emphasize the necessity of better water quality control practices along with enhanced sanitation procedures which must be executed specifically during the rainy season to reduce health risks from surface water faecal contamination.

4.2.3 Relationship between Bacteriological Parameters and Physicochemical Parameters

During the dry season the total coliform count generally in all sampling points had a positive correlation with electrical conductivity (R=0.0653), turbidity (R=0.240), temperature (R=0.251), TDS (R=0.7005), TSS (R=0.4245), nitrates (R=0.8839) and phosphates (R=0.2759) while had a negative correlation with dissolved oxygen (R=-0.0162,) and pH (R=-0.226) (Table 4.5). On the other hand, the faecal coliforms generally has a positive correlation with electrical conductivity (R=0.395), turbidity (R=0.4998), temperature (R=0.4032), TDS (R=0.6417), TSS (R=0.4872), nitrates (R=0.5749) and phosphates (R=0.3638) while a negative correlation with dissolved oxygen (R=-0.2362) and pH (R=-0.446,) (Table 8).

Table 8: Spearman correlation coefficients for physical parameters during dry season

Spearman Prob > r under H0: Rho=0 dry season	Correlation Coefficients, N = 36								
	Cond	Turb	DO	pH	Temp	TDS	TSS	NO ₃	PO ₄
Tocoli	0.065	0.240	-0.016	-0.226	0.251	0.701	0.425	0.884	0.276
Dry	0.705	0.158	0.925	0.185	0.139	<0.001	0.009	<0.001	0.103
Fecoli	0.395	0.499	-0.236	-0.447	0.403	0.642	0.487	0.575	0.364
Dry	0.017	0.002	0.165	0.006	0.015	<0.001	0.003	0.002	0.029

The research by Town and Ethiopia (2025), supports findings in this study which show positive relationships between coliform counts and electrical conductivity, turbidity, temperature, total dissolved solids (TDS), total suspended solids (TSS), nitrates, and phosphates because such environmental factors make water bodies more favorable for bacterial growth. The presence of elevated turbidity along with TSS creates surfaces where bacteria can effectively attach to grow because of its ability to provide adherence points (Mitova, 2025). Research by Soares *et al.* (2025), supports the survival of fecal coliforms during times of low DO levels and high pH because their findings demonstrate that such environmental conditions result in elevated organic pollution. The growth of bacteria becomes less favorable under alkaline conditions which explains the decreased coliform counts. According to Ibrahim (2025), eutrophication develops when nitrates and phosphates from agricultural runoff reach excessive levels which promotes coliform bacterial growth. The coliform bacteria concentration grows higher throughout water bodies as dry seasons create lower water flow conditions.

During the wet season the total coliform count generally in all the sampling points had a positive correlation with the electrical conductivity (R=0.388), turbidity (R=0.480), temperature (R=0.539), total dissolved solids (R=0.568), total suspended solids (R=0.395) nitrates (R=0.421) and phosphates (R=0.205) while a negative correlation with dissolved oxygen (R=-0.016) and pH (R=-0.226) (Table 4.9). On the other hand, the faecal coliforms generally had a positive correlation with electrical conductivity (R=0.399), turbidity (R=0.5462), temperature (R=0.422), TDS (R=0.671), TSS (R=0.507), nitrates (R=0.574) and phosphates (R=0.387) while had a negative correlation with Dissolved oxygen (R=-0.2148) and pH (R=-0.452) (Table 9).

Table 9: Spearman correlation coefficients for physical parameters during wet season

Spearman Prob > r under H0: Rho=0	Correlation		Coefficients,		N	=	36	wet season	
	Cond	Turb	DO	pH				Temp	TDS
Tocoli_wet	0.387	0.480	-	-	0.539	0.568	0.394	0.421	0.205
	0.019	0.003	0.347	0.491	0.007	0.003	0.017	0.010	0.230
Fecoli_wet	0.398	0.546	-	-	0.422	0.671	0.506	0.573	0.387
	0.015	0.006	0.215	0.452	0.010	<0.001	0.001	0.003	0.019
			0.208	0.005					

Other studies confirm this bacteriological and physicochemical parameter relationship that demonstrates seasonal water quality variations. The findings by Islam *et al.* (2024), about Tasik Chini Malaysia, support the positive correlations between total and fecal coliforms and electrical conductivity, turbidity, temperature, TDS, TSS, nitrates, and phosphates. The combination of high TDS and TSS levels signals that sediment and runoff materials exist which allow bacteria to attach while providing essential nutrients for growth.

The streams of Darjeeling India experienced enhanced microbial activity because of wet season temperature elevation and turbidity increases (Bhutia, 2024). Warmer water temperatures boost bacterial metabolism thus leading to elevated coliform counts according to the study results. Research by Tadeu *et al.* (2024), validated the positive relationship between nitrates and phosphates and microbial growth in the Doce River Basin during the rainy season. The research findings showing negative effects on dissolved oxygen (DO) and pH in this study match previous recorded results. Tecklie (2024), explained that elevated bacterial concentrations reduce water oxygen levels because decomposing organic matter requires oxygen from bacterial respiration activities. Athulya *et al.* (2025), stated that lower pH values in the rainy period enable coliform bacteria to survive through runoff and increased organic acid concentrations.

4.3 Characterization of the Adsorbents

4.3.1 FTIR spectra of Tea Waste Hydrochar/MWCNTs Composite

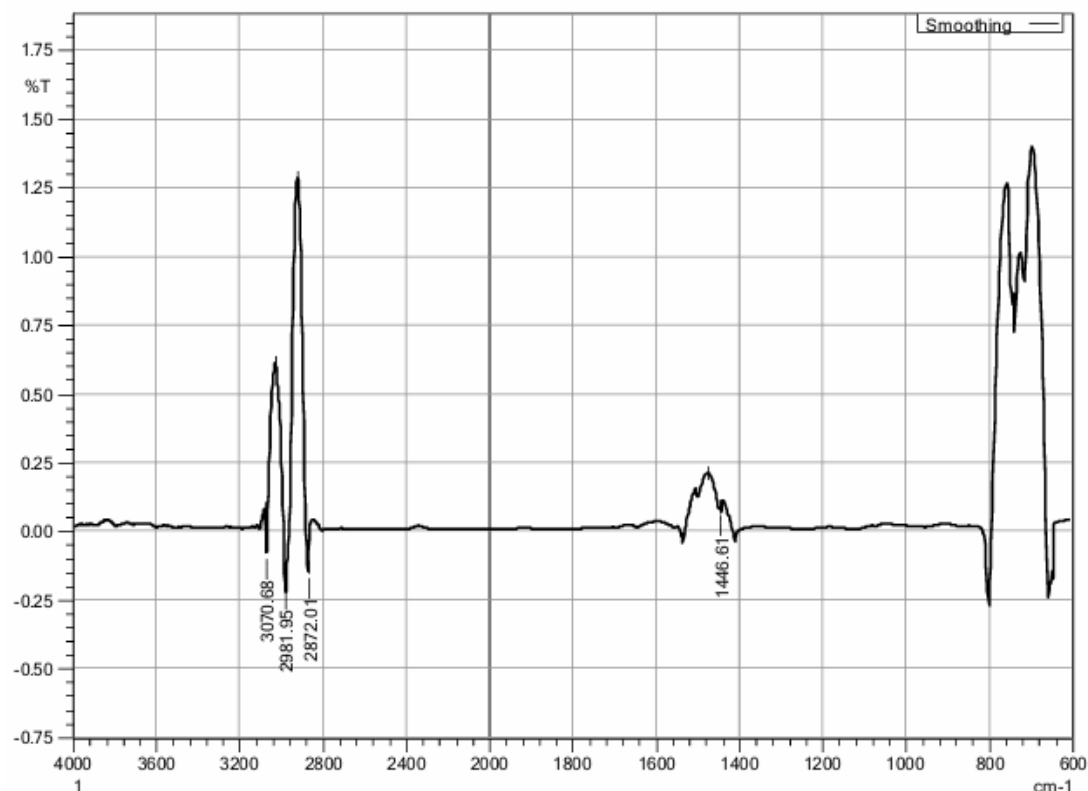


Figure 5: FTIR spectrum of hydrochar of tea waste/MWCNTs composite A

The FTIR spectrum for the 0.99:0.01 ratio tea waste hydrochar/MWCNTs composite A is shown in figure 5. The peak at 3070.88 cm^{-1} represents C–H stretching from aromatic rings which stems from tea polyphenols alongside lignin (Ateş *et al.*, 2023). Absorptions at 2872.01 cm^{-1} and 2981.95 cm^{-1} was assigned to asymmetric and symmetric $-\text{CH}_3/-\text{CH}_2$ stretching which indicates aliphatic chains found in lignocellulosic biomass (Ye *et al.*, 2022 ;Moreno-Bermedo *et al.*, 2025). The 1446.61 cm^{-1} signal shows both $-\text{CH}_2$ bending and C=C skeletal vibrations which indicate stability in aromatic carbon arrangements (Tripathi *et al.*, 2023).

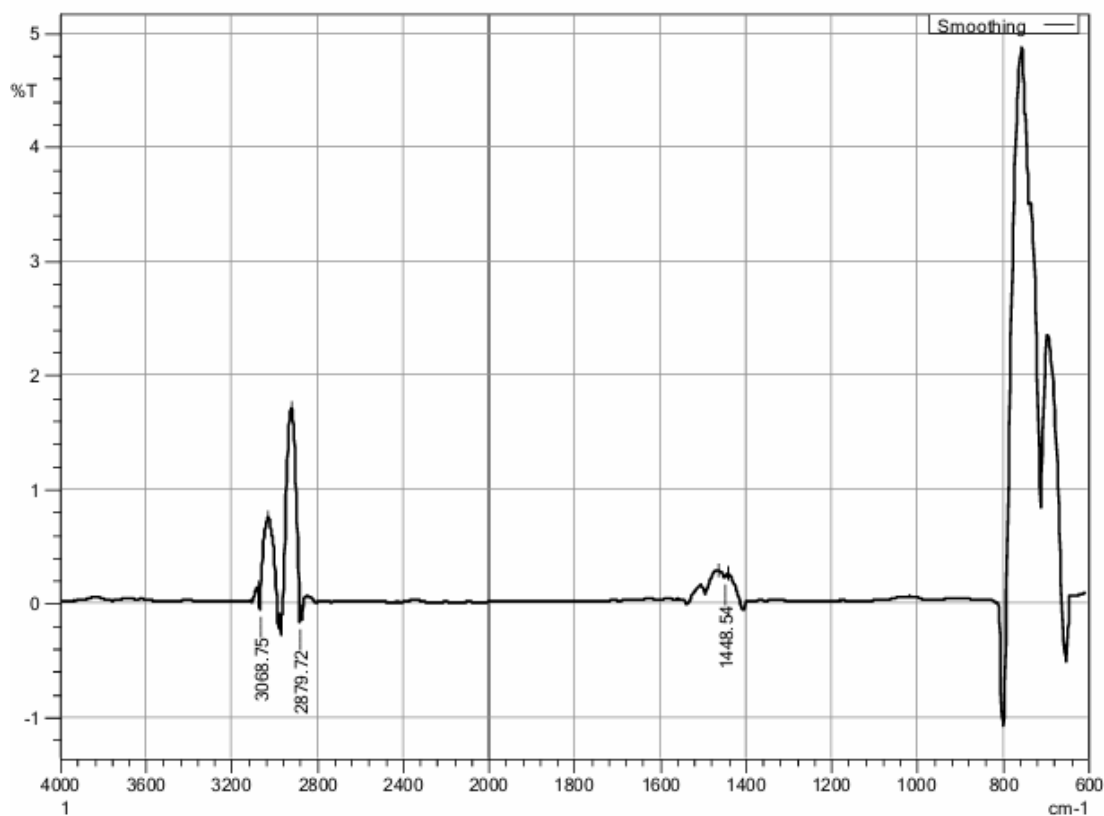


Figure 6: FTIR spectrum of hydrochar of tea waste/MWCNTs composite B

Analysis of the FTIR spectrum for the tea waste hydrochar/MWCNTs composite B with ratios of 0.99:0.02 (figure 6), shows comprehensive information about surface chemical interplay and functional group bond formation. The FTIR spectrum shows three vital peaks at 3088.75 cm^{-1} and 2879.72 cm^{-1} and 1448.54 cm^{-1} which indicate aromatic $=\text{C}-\text{H}$ stretching while the aliphatic $-\text{CH}$ stretching arises from $-\text{CH}_3/-\text{CH}_2$ groups and both $\text{C}-\text{H}$ bending and $\text{C}=\text{C}$ skeletal vibrations exist in this sample (Moreno-Bermedo *et al.*, 2025). These peaks indicate partial carbonization with retention of lignin, cellulose, and phenolic structures (Tripathi *et al.*, 2023; Ateş *et al.*, 2023).

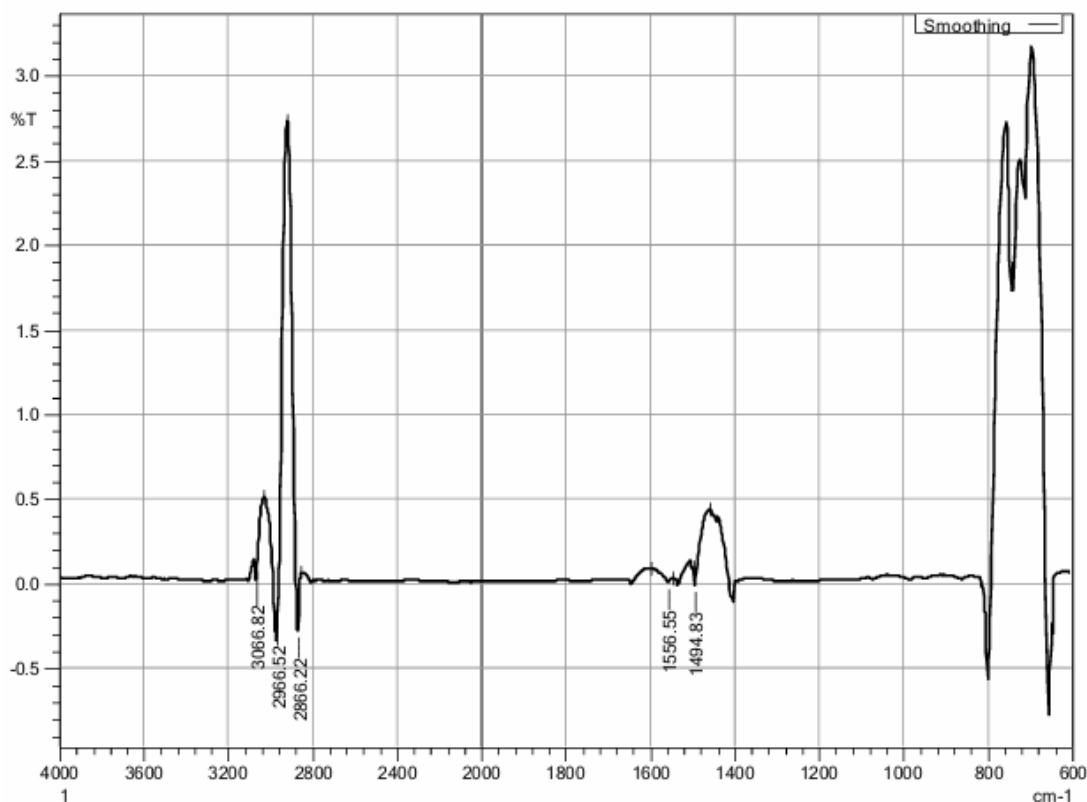


Figure 7: FTIR spectrum of hydrochar of tea waste/MWCNTs composite C

The FTIR spectroscopy of tea waste hydrochar/MWCNTs composite (0.97:0.03 weight ratio) is shown in figure 7. The peak at 2956.52 cm^{-1} and 2866.62 cm^{-1} indicate the asymmetric and symmetric stretching vibration of $-\text{CH}_3$ and $-\text{CH}_2-$ groups that are typical for aliphatic hydrocarbons found in lignocellulosic biomass materials (Tripathi *et al.*, 2023). Aromatic C=C stretching band at 1556.55 cm^{-1} indicate presence of lignin structures or aromatic domains present in hydrothermal carbonization processes (Ateş *et al.*, 2023). The aromatic structure of hydrochar is confirmed by 1494.83 cm^{-1} band which indicates partial graphitization properties (Ye *et al.*, 2022 ;Moreno-Bermedo *et al.*, 2025).

4.3.2 XRD Spectra of Tea Waste Hydrochar/MWCNTs Composite

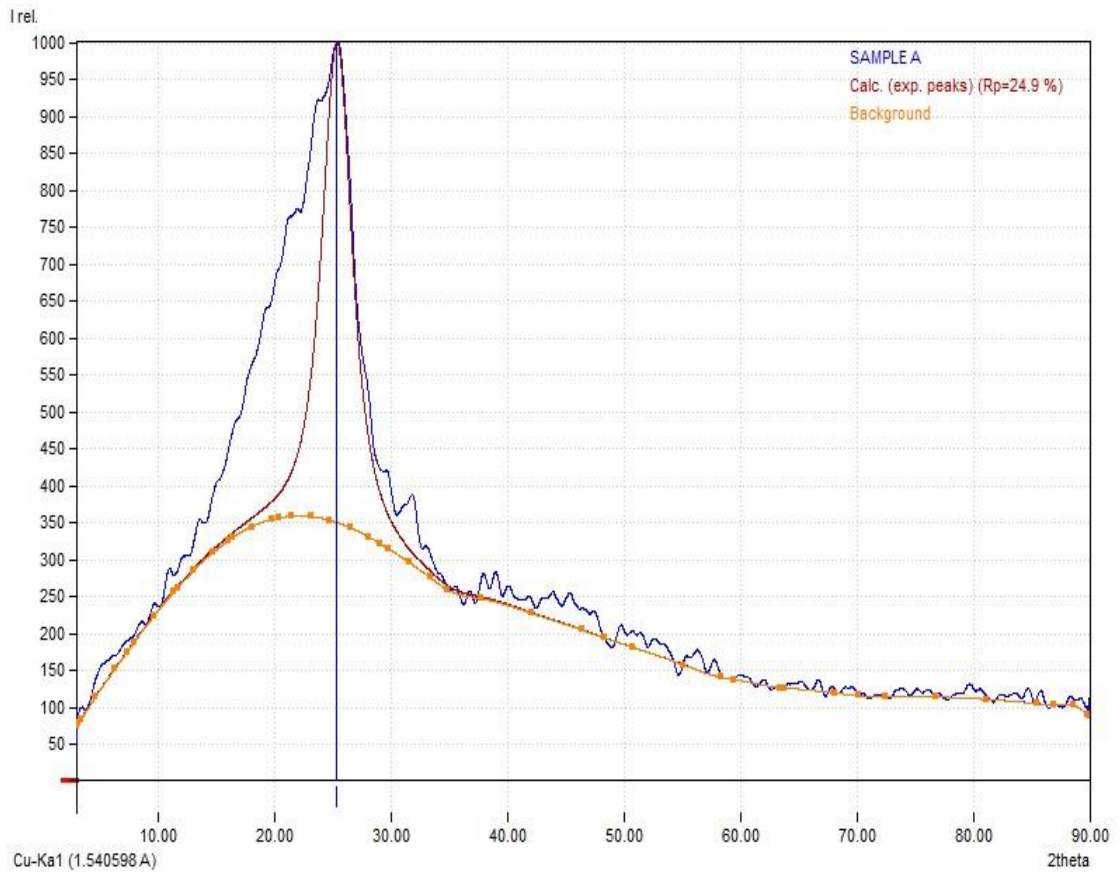


Figure 8: XRD spectrum of hydrochar of tea waste/MWCNTs composite A

The X-ray diffraction pattern of the tea waste hydrochar/MWCNTs composite A (0.99:0.01 ratio) is shown in figure 8. The X-ray diffraction peak at $2\theta=26^\circ$ indicate presence of graphitic carbon crystalline structure of MWCNTs (002) planes (Saputra *et al.*, 2023;. The wide hump between $2\theta =15^\circ-30^\circ$ shows amorphous carbon from hydrochar of tea waste (Moreno-Bermedo *et al.*, 2025).

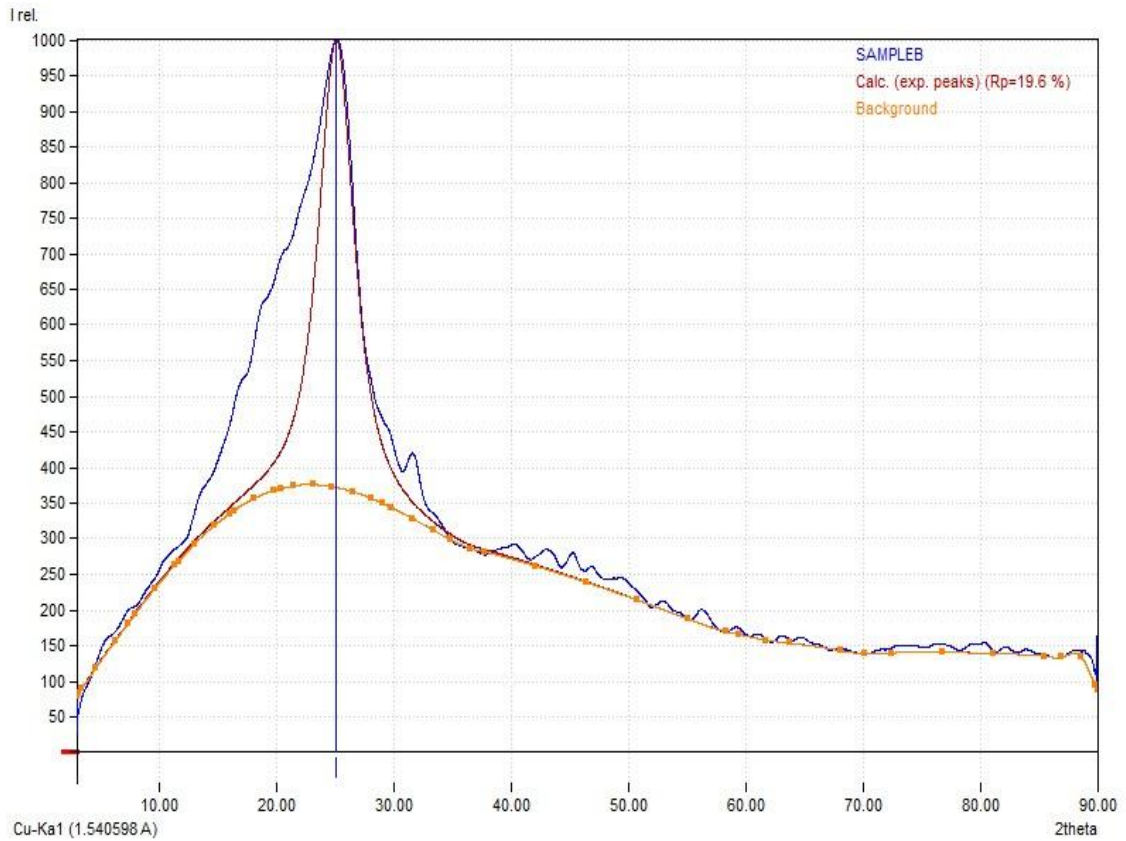


Figure 9: XRD spectrum of hydrochar of tea waste/MWCNTs composite B

X-ray diffraction (XRD) pattern of tea waste hydrochar/MWCNTs composite B at the weight ratio of 0.98:0.02 is shown in figure 9. The broad peak at $2\theta=25.14^\circ$ indicate carbonaceous structure from amorphous disorder characteristic of tea waste biochar lignocellulosic material and graphitic carbon crystalline structure of MWCNTs (002) planes (Borah *et al.*, 2012 ;Saputra *et al.*, 2023; Moreno-Bermedo *et al.*, 2025).

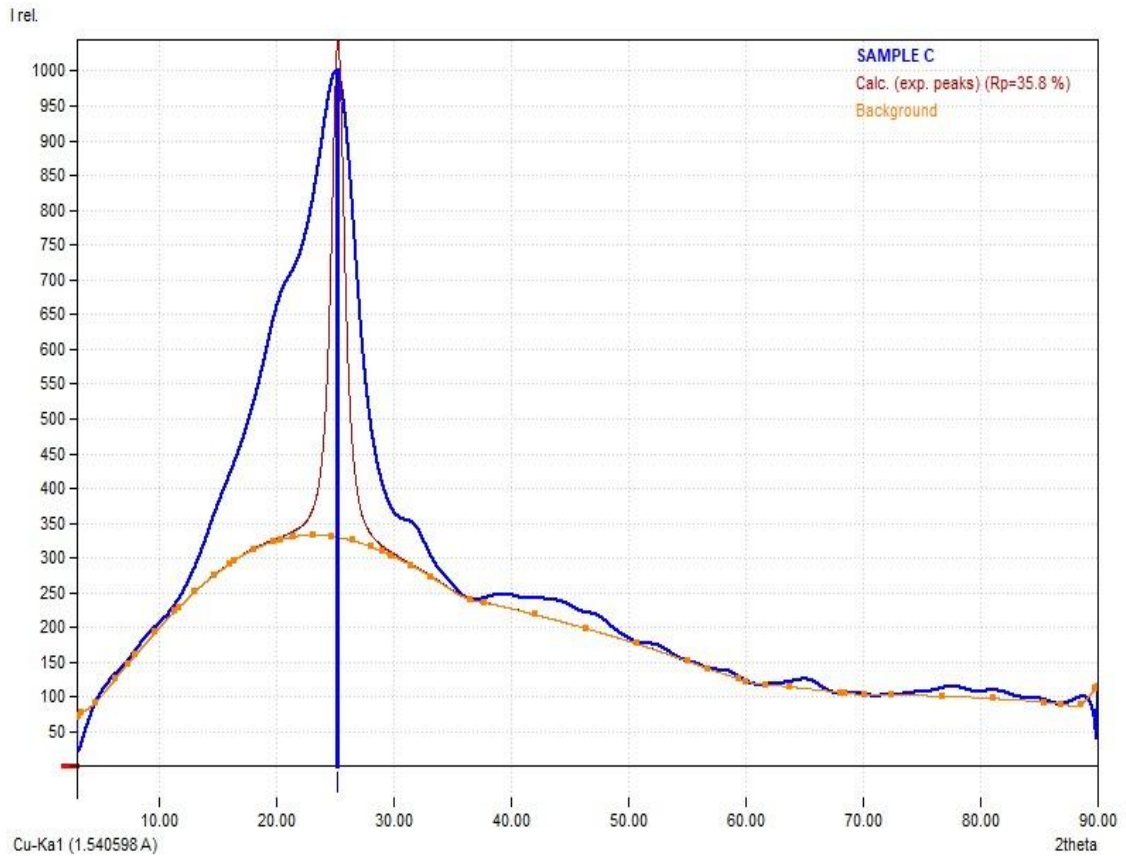


Figure 10: XRD spectrum of hydrochar of tea waste/MWCNTs composite C

XRD spectrum of tea waste hydrochar/MWCNTs composite C (0.97:0.03 weight ratio) is shown in figure 10. The spectrum displayed one distinct peak at $2\theta = 25.28^\circ$ which shows a carbonaceous structure from amorphous disorder characteristic of tea waste biochar lignocellulosic material and graphitic carbon crystalline structure of MWCNTs (002) planes (Moreno-Bermedo *et al.*, 2025; Saputra *et al.*, 2023)

4.4 Adsorption Experiments of Copper (II) Ions

4.4.1 Effect of Adsorbent Dosage on Adsorption of Cu (II) Ions

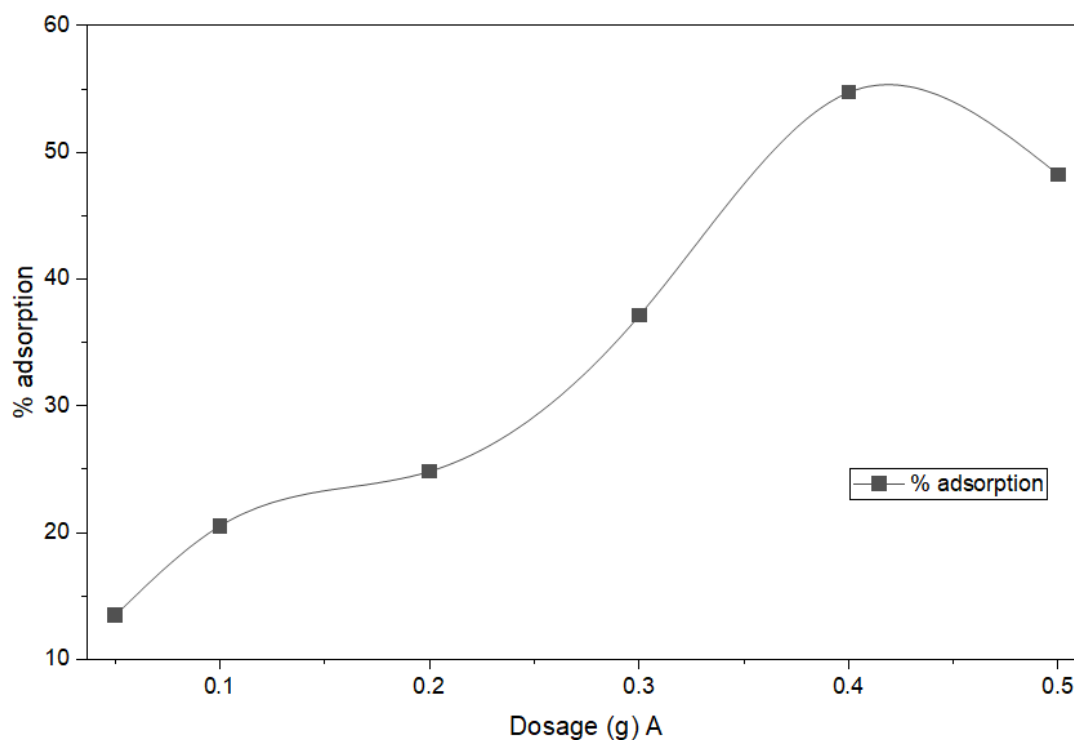


Figure 11: Effect of adsorbent dosage on adsorption of Cu (II) ions (composite A)

The % adsorption values for Composite A progressively rose from about 14% until it reached 20.5% at a 0.1 g dosage of adsorbent as shown in figure 11. Increase in dosage led to a substantial rise in adsorption performance and a maximum of 55% was achieved at 0.4 g. The increase in adsorption efficiency occurred because additional available active sites that can bind Cu (II) ions were added (Fei & Hu, 2022). Further increase in dosage to 0.5 g led to decrease in adsorption as a result of supersaturation and overlapping of sorption sites (Rezania *et al.*, 2024).

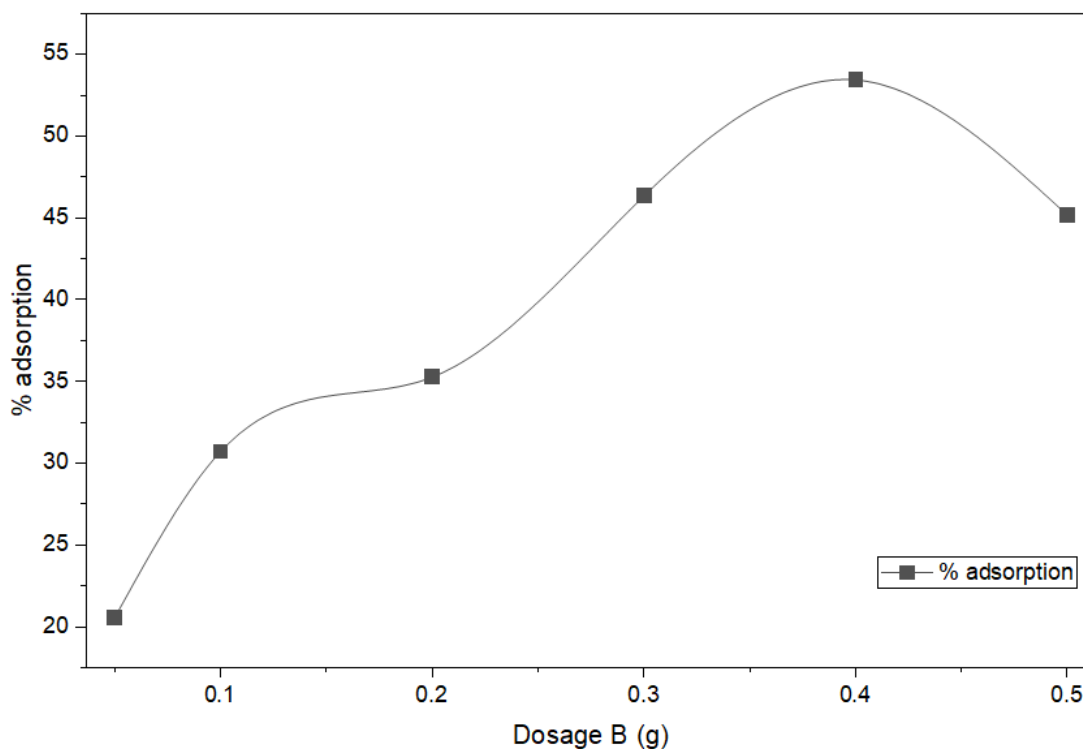


Figure 12: Effect of adsorbent dosage on adsorption of Cu (II) ions (composite B)

The adsorption efficiency of Composite B reached 53% quickly after adding 0.1 grams then decreased at 0.2 to 0.3 grams and rose again when dosage was increased to 0.4 grams until it reached 50% efficiency (figure 12). The higher sorption capacity resulted from higher MWCNT content which increased the adsorption area and capacity as compared to composite A (Gupta *et al.*, 2017). The intermediate dosage range in the experiment demonstrates findings similar to those described by Raji *et al.* (2023), because high amounts of MWCNTs may block or clap active sites thus decreasing system efficiency. The improved adsorption capacity at higher dose levels occurs because better dispersion exposure allows active sites to become available again (Wu *et al.*, 2018).

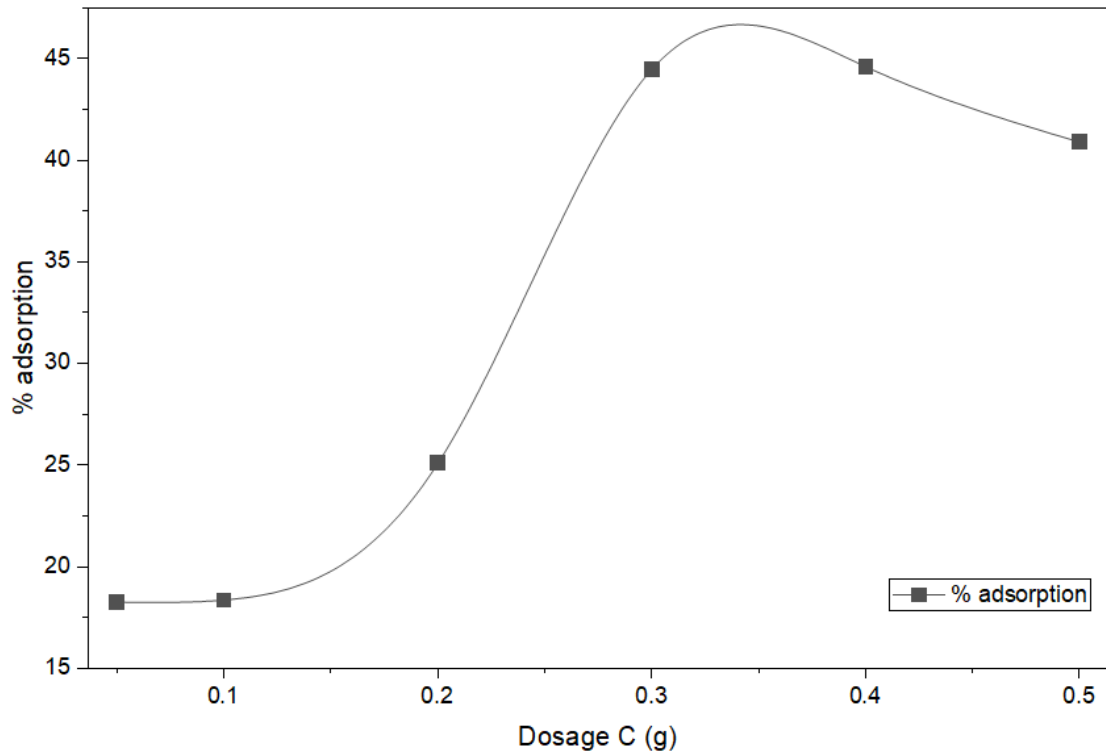


Figure 13: Effect of adsorbent dosage on adsorption of Cu (II) ions (composite C)

The adsorption output of Composite C increased proportionally with added adsorbent mass and attained its maximum value of 45% at 0.4 g then demonstrated a minimal decrease (figure 13). The enhanced MWCNT concentration level of 0.03 led to superior adsorption capabilities because of its increased surface area together with functional groups that boosted Cu (II) ion binding (Zhang *et al.*, 2024). Higher concentrations of the adsorbent led to decrease in effectiveness due to particle-aggregated suspension which creates fewer available active sites (Yang & Jiang, 2014).

The experimental data obtained through all composite studies shows adsorption behavior that conforms to various studies which indicate that increasing the dosage of adsorbents leads to improved % adsorption until the saturation point is achieved (Gupta *et al.*, 2017; Raji *et al.*, 2023) After reaching the optimal dosage threshold both particle agglomeration effects and competition among sites can hinder the adsorption efficiency (Wu *et al.*, 2018; Fei & Hu, 2022). The research conducted by Zhang *et al.* (2024), supports the improved adsorption capacity of materials which contain higher MWCNT levels in examinations that used Composite C followed by Composite B and then Composite A.

4.4.2 Effect of Initial Metal Concentration on Adsorption

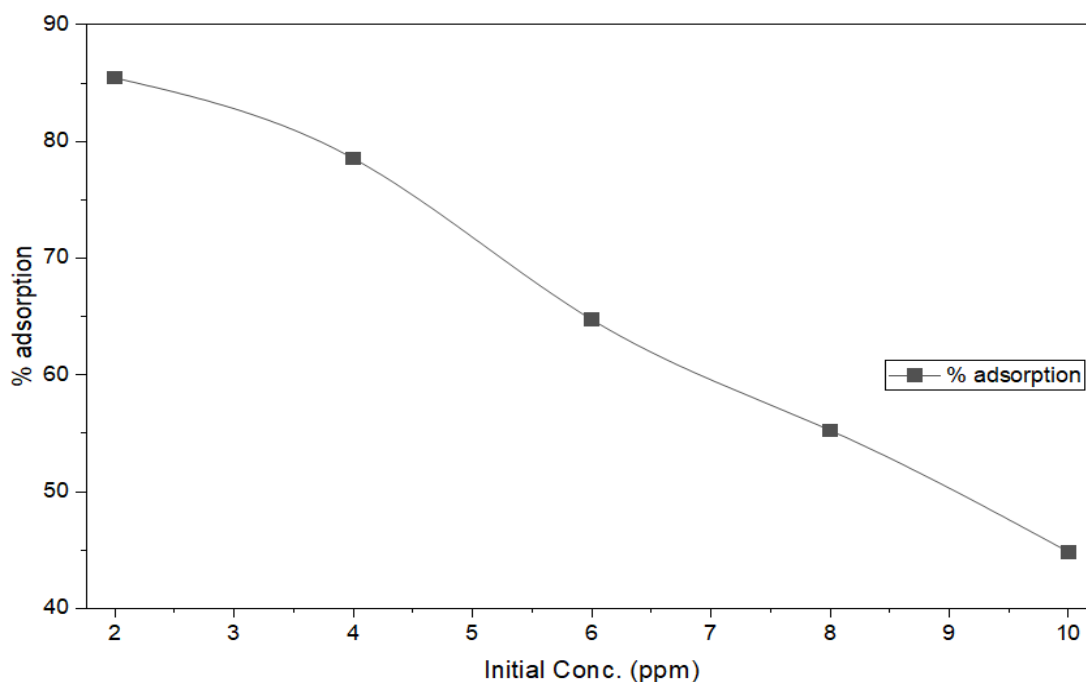


Figure 14: Effect of initial metal concentration on adsorption of Cu (II) ions

The adsorption percentage reduced substantially between 6 and 8 ppm Cu (II) until it hits its minimum point at 30% at the 8-ppm concentration mark. The adsorption efficiency decreased because the available adsorption sites on the composite became progressively saturated thus reducing its capacity to bind more metal ions. The process of electrostatic repulsion contributes to decreased adsorption tendencies since Cu (II) ions that previously bound to the composite surface maintain a repulsive force that prevents additional ions from binding (Dichiara *et al.*, 2015).

The carbon nanotube/hydrochar tea composite shows an appreciable response to the initial concentration of Cu (II) ions which exist in solution. Figure 14 shows an irregular adsorption percentage pattern where higher concentrations of Cu (II) result in declining outcomes but reach maximum values at very high concentrations. The maximum sorption capacity was recorded at 2 ppm (85%) due to availability of sorption sites and decreased as the concentration of copper (II) ions increased as a result of competition of active sites as more ions were added to the solution. The composite material possesses adequate active sites during low metal ion exposure which facilitates effective metal adsorption on its surface. Mass transfer of Cu (II) ions to the adsorbent surface becomes more efficient due to the high solution to adsorbent concentration

gradient. A study conducted by Gupta *et al.* (2015), revealed that unoccupied binding sites on carbon-based adsorbents achieve maximum adsorption efficiency when metal ions exist at low concentrations.

4.4.3 Effect of Contact Time on Adsorption of Cu (II) Ions

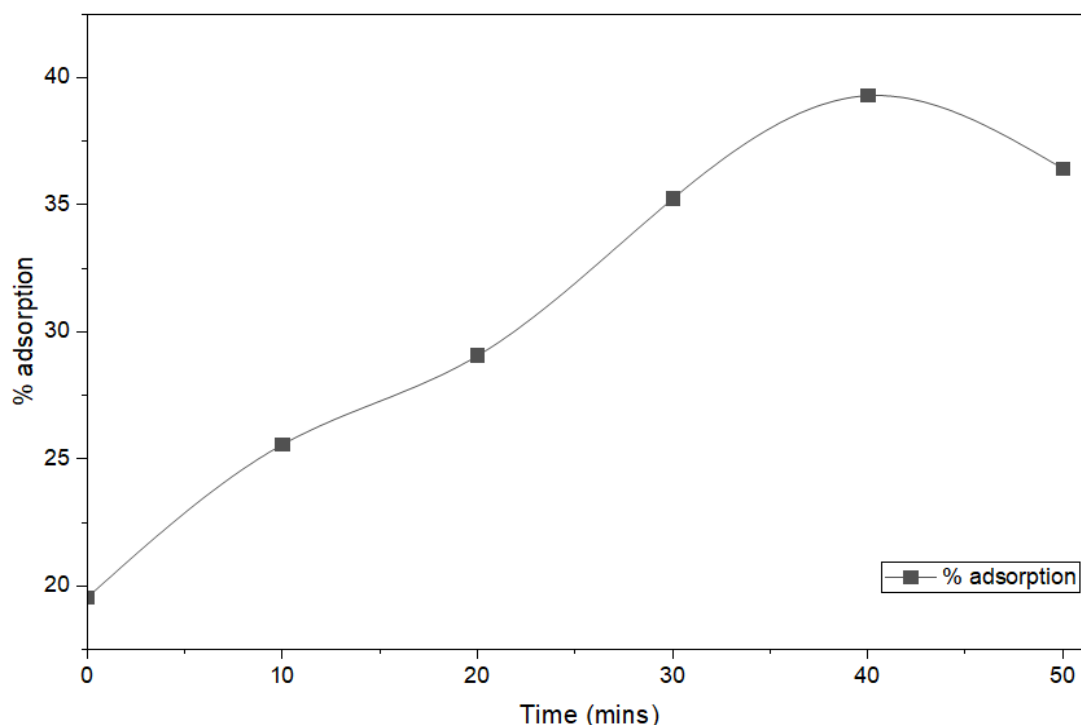


Figure 15: Effect of contact time on adsorption of Cu (II) ions

The contact period between carbon nanotube/hydrochar composites and Cu (II) ions determines both adsorption efficiency and equilibrium uptake. The adsorption efficiency increased with increasing contact time from 20-39% at 0-40 mins). The microporous structure of hydrochar enables Cu (II) ion diffusion which allows them to bond with hydroxyl and carboxyl groups (Wan & Li, 2015; Ewis & Hameed, 2021). The maximum sorption capacity was reported at 40 mins (39%) as contact time increased the adsorption decreased to 36% at 50 mins (figure 15). The decrease was due to supersaturation of active sites. The adsorption process of biochar-based nanocomposites attains equilibrium at 40-50 minutes and reaches 65-75% efficiency (Yang *et al.*, 2019). The maximum adsorption capacity of 80-90 mg/g for Cu (II) was achieved by functionalized hydrochar composites depending on surface modifications alongside solution conditions (Khanzada *et al.*, 2024). The synthesis parameters and functional group modifications require optimization because they boost adsorption

capabilities while extending adsorption stability (Xia *et al.*, 2019).

4.4.4 Effect of Temperature on Adsorption of Cu (II) Ions

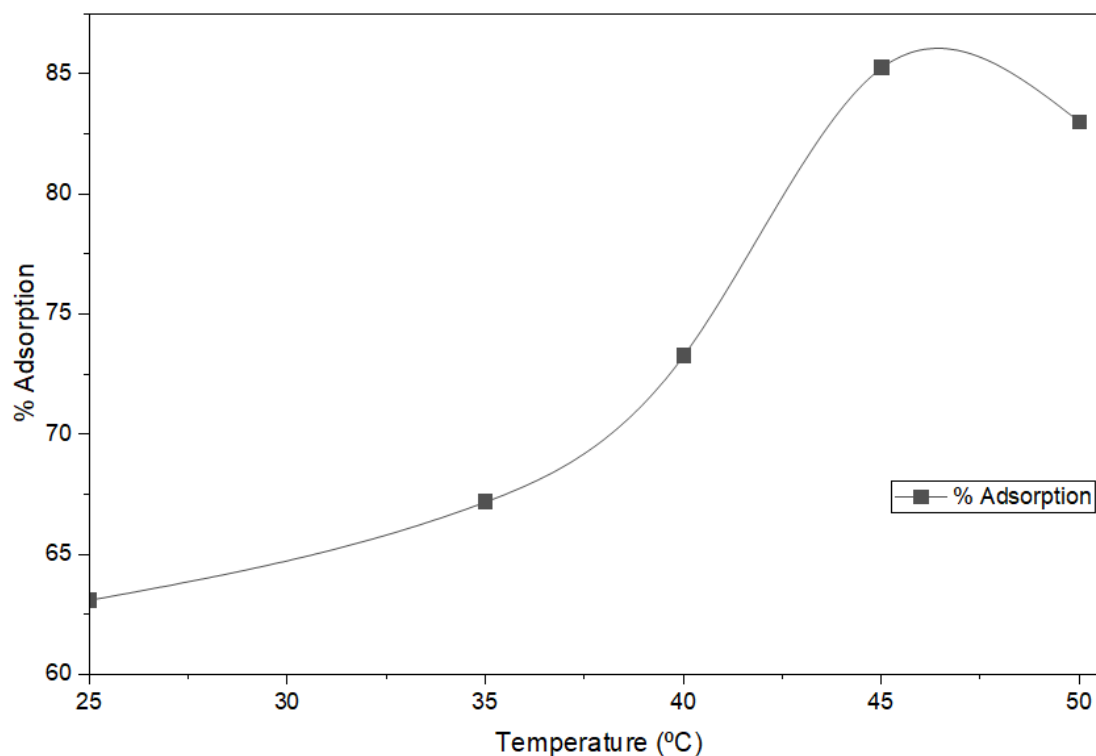


Figure 16: Effect of temperature on adsorption of Cu (II) ions

Increasing temperature from 25-45°C increased the adsorption capacity of Cu (II) from 63-85% as shown in figure 16. The binding of Cu (II) ions onto the adsorbent surface shows endothermic behavior since elevated temperatures optimize the adsorption process. Adsorption of Cu (II) ions exhibits stronger affinity to the adsorbent at elevated temperatures because heat stimulates surface activity and accelerates Cu (II) diffusion and creates additional adsorbing sites. Adabi *et al.* (2023), demonstrated that increase in temperature improved Cu (II) adsorption because better ion motion combines with stronger binding of surface functional groups on the adsorbent. Zhang *et al.* (2024), studied the adsorption of Cu (II) using biochar-based adsorbents and found that higher temperatures led to enhanced adsorption efficiency because of increased porosity together with expanded micropore dimensions in the adsorbent structure. The research by Khanzada *et al.* (2024), demonstrated that Cu (II) adsorption occurs endothermically through the positive determination of enthalpy change (ΔH°) thermodynamic parameter which indicates better adsorption occurs at elevated temperatures.

The adsorption efficiency showed its highest point at 45-50°C range which might be related to the lowered activation barriers which enabled better ion transport. At elevated temperatures the desolvation effects strengthen because Cu (II) ions remove water molecules from their structure and better connect to the surface of the adsorbent. High temperature conditions can cause modifications in adsorbent material structure as well as metal ion loss which exceeds the acceptable operational framework. Wang *et al.* (2021), reported that adsorption achieved its peak at approximately 60°C then reached equilibrium point or started decreasing because of existing desorption processes.

4.4.5 Effect of pH on Adsorption of Cu (II) Ions

The adsorption capacity of Cu (II) ions using MWCNTs/ tea waste hydrochar is shown in figure 17. Low adsorption capacity was recorded at pH 2 with 25% capacity. The variation between surface charges and metal ion forms and active chemical group attachment points determines the pH shift. Low pH values below 4 prevent efficient Cu (II) ion adsorption because the surplus H⁺ ions occupy binding sites on the MWCNTs/hydrochar composite (Rezania *et al.*, 2024). The excessive number of protons in the solution protonates hydroxyl and carboxyl functional groups which then lose their binding capacity for Cu (II) ions (Elboughdiri *et al.*, 2024). At elevated pH levels the deprotonated functional groups on the composite surface increase the electrostatic attraction towards positively charged Cu (II) ions which improves adsorption efficiency.

At a pH of 6 the adsorption increased because the divalent Cu (II) ions exist predominantly while effectively binding to active sites on the composite system (Chen *et al.*, 2019). When the solution pH exceeded 7 there was reduction in the amount of adsorbate bound to the composite material. The formation of insoluble Cu (OH)₂ causes decreased available Cu (II) ions to bind with the composite surface (Yang *et al.*, 2019). The adsorption sites become increasingly occupied by hydroxide ions during alkaline conditions thus leading to reduction in adsorption efficiency of Cu (II) ions (Zhou *et al.*, 2022).

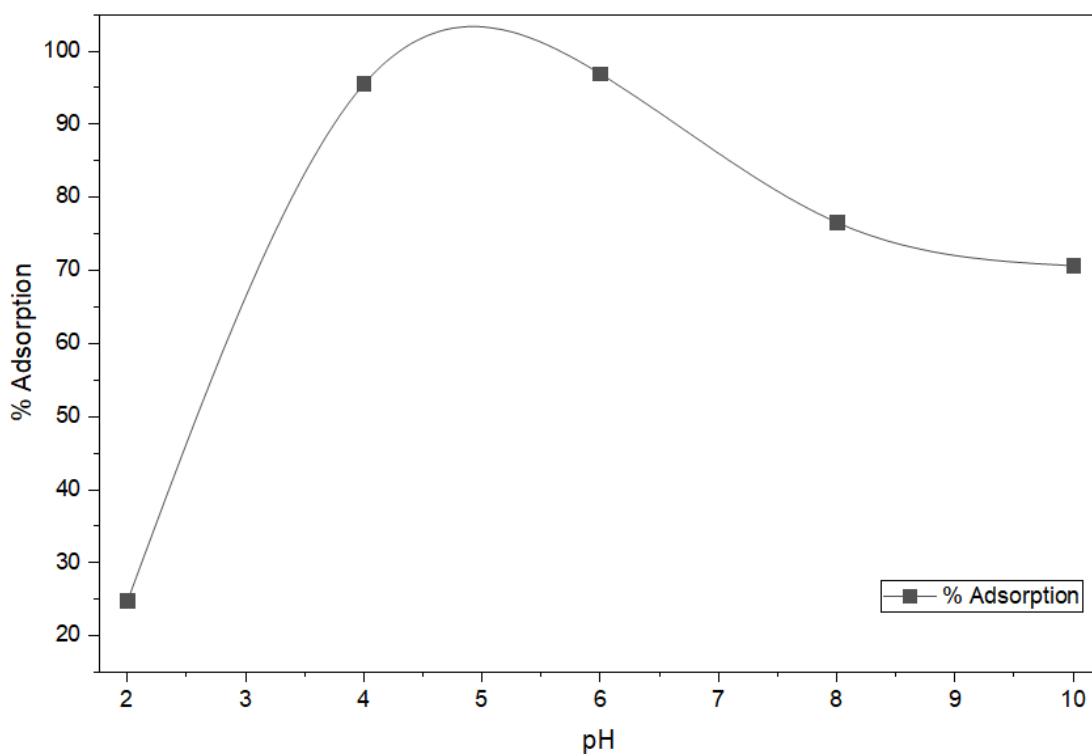


Figure 17: Effect of pH on adsorption of Cu (II) ions

4.5 Kinetic Studies for Adsorption of Cu (II) Ions

The kinetic analysis of Cu (II) ion adsorption using MWCNTs/tea waste hydrochar employed both pseudo-first-order and pseudo-second-order evaluation approaches as shown in figure 18 and 19 (table 4.10). The analysis showed that MWCNTs and hydrochar tea waste system had a pseudo-first-order rate constant ($K_1 = 0.1945 \text{ min}^{-1}$) and an equilibrium adsorption capacity ($Q_e = 0.0728 \text{ mg/g}$) together with a correlation coefficient ($R = 0.92478$). The pseudo-second-order model fitting produced a rate constant (K_2) of 3.8659 g/mg.min along with an equilibrium adsorption capacity (Q_e) of 0.07857 mg/g . It showed a better correlation coefficient ($R = 0.98863$) than the pseudo-first-order model. The valid fit of the pseudo-second-order model demonstrates that valence forces as well as electron sharing between Cu (II) ions and MWCNTs/hydrochar functional groups determine the main mechanism which ruled the adsorption process.

The research of Sun and Wang (2006), validated the usage of the pseudo-second-order model to analyze Cu (II) absorption onto N, O-carboxymethyl-chitosan indicating that chemisorption functions as a primary factor in heavy metal elimination. The research

of Babalola and Wilson (2024), reviewed the removal efficiency of Cu (II) through composite biowaste adsorbents which include hydrochar and MWCNTs using a similar kinetic mechanism. MWCNTs exhibit notable surface area accessibility and functionalization properties according to Sheraz *et al.* (2024), which leads to superior heavy metals removal capacity. This indicate that pseudo-second-order kinetics dominated which shows that chemical processes governed the adsorption mechanism.

Table 10: Pseudo first and second order kinetics constants for Cu (II) ions adsorption

Pseudo first order			Pseudo second order		
K_1	Q_e	R	K_2	Q_e	R
0.0411min^{-1}	0.0786mg/g	0.93615	3.8659g/mg.min	0.07857mg/g	0.9774

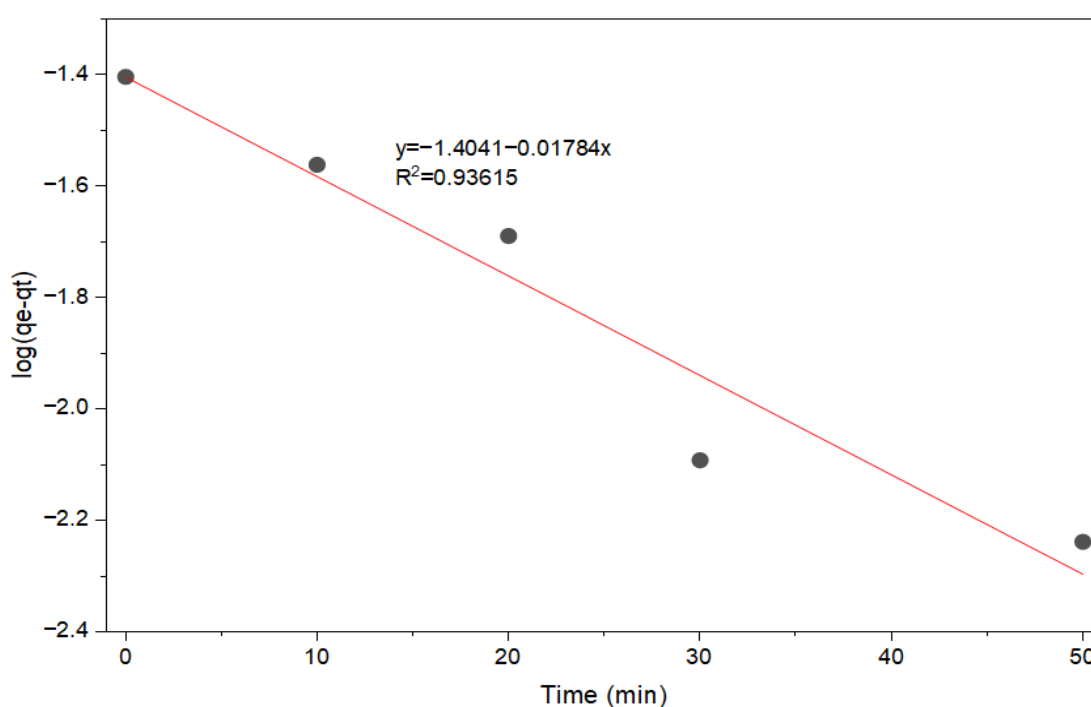


Figure 18: Pseudo First Order Kinetics of Cu (II) Ions Adsorption

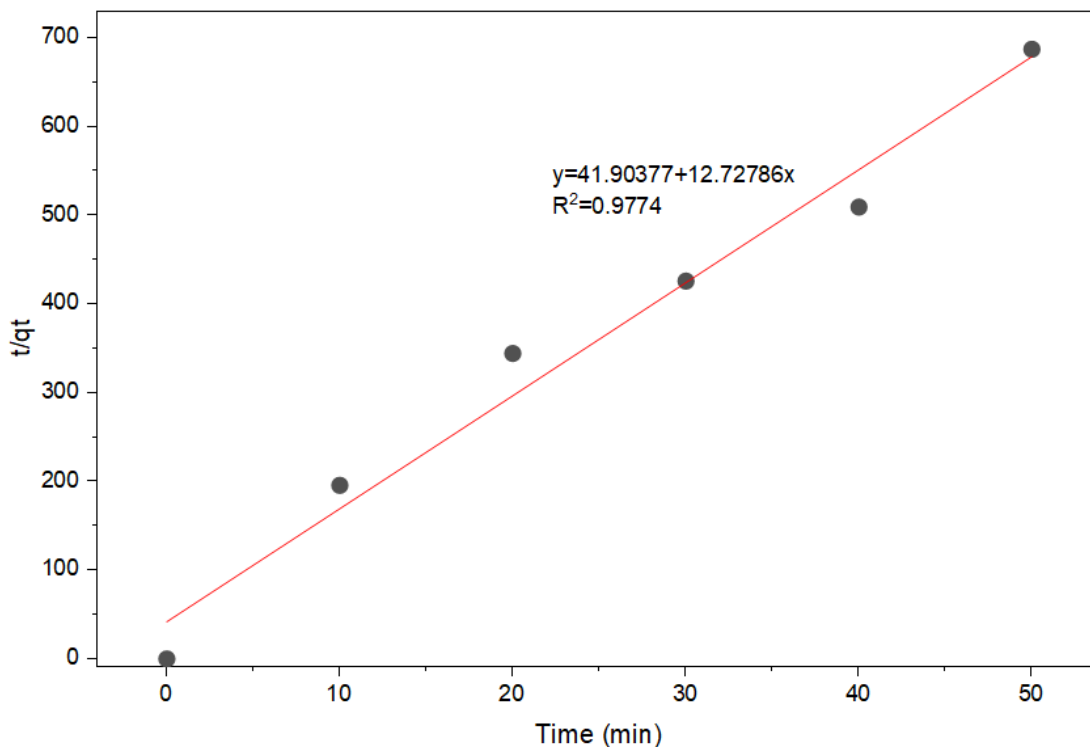


Figure 19: Pseudo second order kinetics of Cu (II) ions adsorption

4.6 Adsorption Isotherms for Cu (II) Ions

The research examined Cu (II) ion adsorption using MWCNTs combined with hydrochar derived from tea waste while applying Langmuir and Freundlich isotherm models for evaluation as shown in figure 20 and 21 (table 4.11). The Freundlich constant KF had a value of 0.1406 mg/g along with n 3.0915 and R of 0.93404, which demonstrates that the adsorption process was highly beneficial because it signifies robust adsorbate-adsorbent bonding and multiple types of adsorption sites. The adsorption process on finite identical sites formed a monolayer according to the Langmuir isotherm parameters where the maximum adsorption capacity was 0.2482 mg/g and the Langmuir constant set at 1.7152 L/mg. Under the examined conditions, the adsorption process was found favorable for Langmuir model which had a (R) value of 0.99529. The research study of Babalola and Wilson (2024), examined the effectiveness of MWCNTs and biowaste-derived hydrochar as composite adsorbents for Cu (II) removal through analysis of their high surface area capability and functionalized active sites. The research by Sheraz *et al.* (2024), indicates that functionalized MWCNTs achieved better metal adsorption because of their natural affinity toward metal ions and followed Langmuir isotherm model for Cd (II) and Cr

(II) ions. Adsorption efficiency tests revealed that hydrochar-based adsorbents achieve better performance comparable to commercial activated carbon derived from agricultural residues or other sources (Cukierman *et al.*, 2019). MWCNTs demonstrate superior Cu (II) removal capabilities compared to traditional biomass-based materials because of their selectable pore channels and intensive electron structure (Abiodun *et al.*, 2023). A review by Fahad *et al.* (2023), revealed that heavy metal ion adsorption improves through hydrochar-functionalized materials because of their oxygen-containing functional groups and follows monolayer adsorption.

Table 11: Freundlich and Langmuir constants for adsorption of Cu (II) ions

Freundlich isotherm			Langmuir isotherm		
KF	n	R	Qmax	KL	R
0.1406mg/g	3.0915	0.93404	0.2482mg/g	1.7152L/mg	0.99529

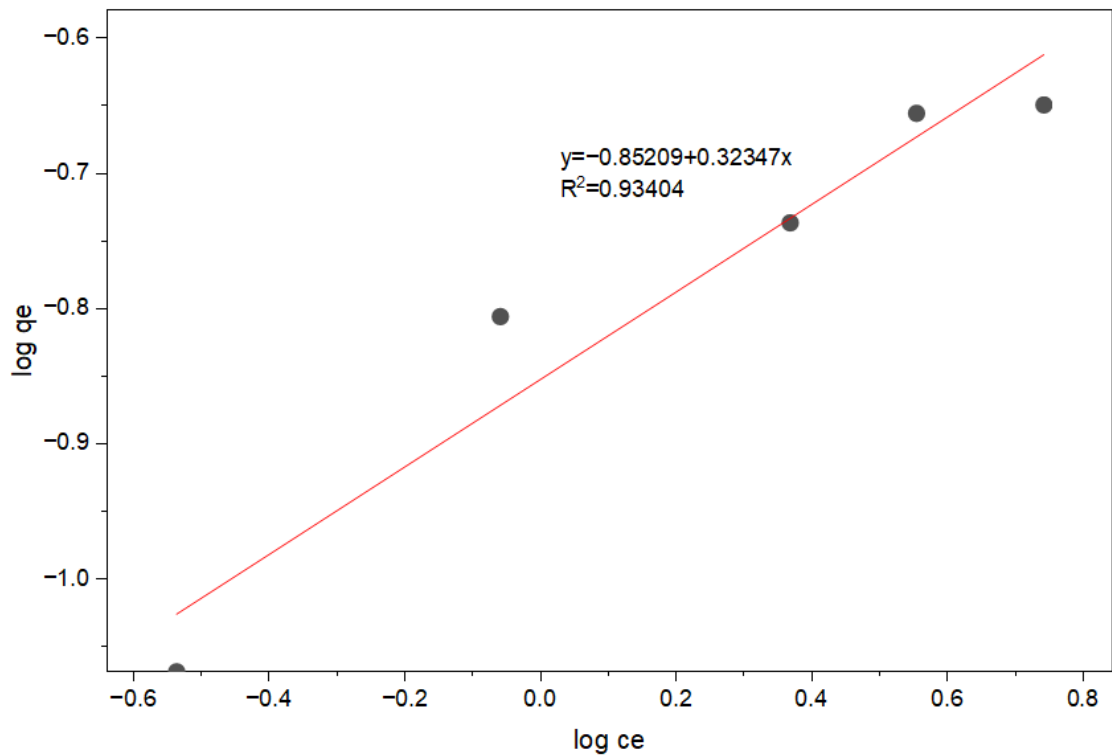


Figure 20: Freundlich isotherm of Cu (II) ions adsorption

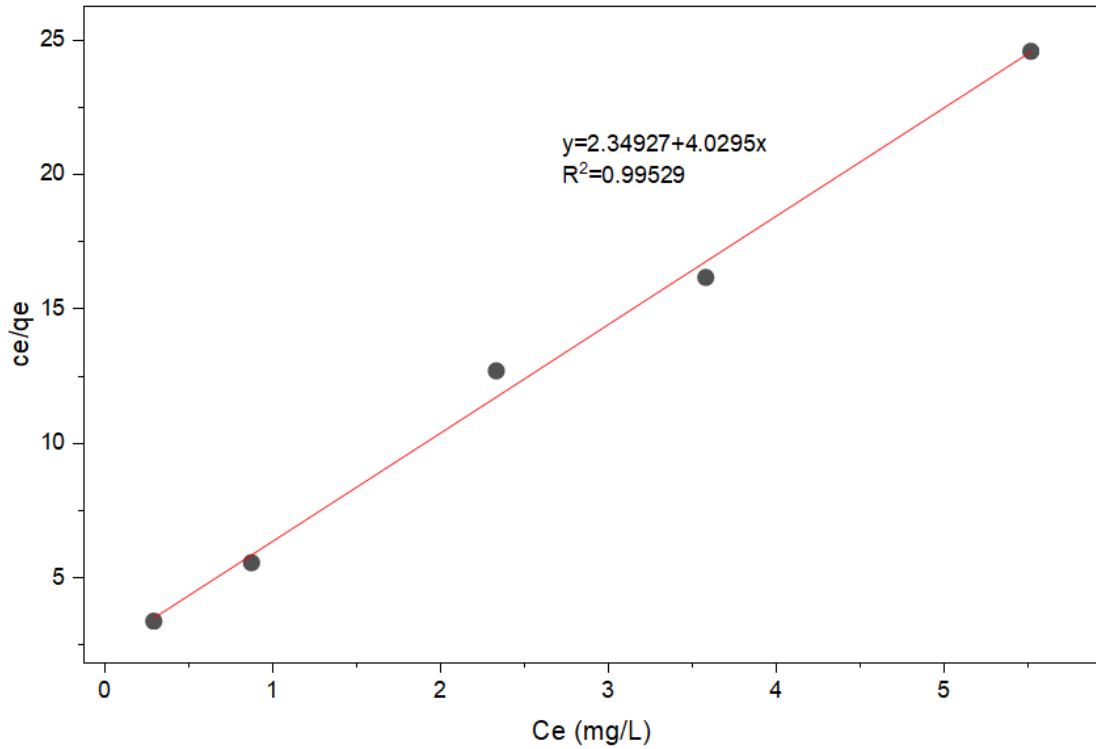


Figure 21: Langmuir isotherm of Cu (II) ions adsorption

4.7 Desorption of Cu (II) ions from Adsorbent Surface

MWCNTs/hydrochar composite achieved more than 99% efficiency in desorbing copper (II) ions within three cycles from the material regardless of the initial metal concentration levels (figure 22). Studies using different metal species including lead (Pb), zinc (Zn), and nickel (Ni) indicate that carbon-based composites retain strong desorption capabilities within their materials structure. The analysis by Kumkum and Kumar (2024), showed that biochar-based adsorbents reached lead ion desorption efficiencies above 98% which indicated effective regenerable and cost-effective operation. Study findings show that modified activated carbon effectively regenerated nickel ions with almost 99% success rates illustrating surface modification techniques enhance heavy metal desorption capabilities (Vakili *et al.*, 2021). Research shows that the opposite process of desorption depends both on metal type and the physical and chemical characteristics of the adsorbent (Kołodzyńska *et al.*, 2017).

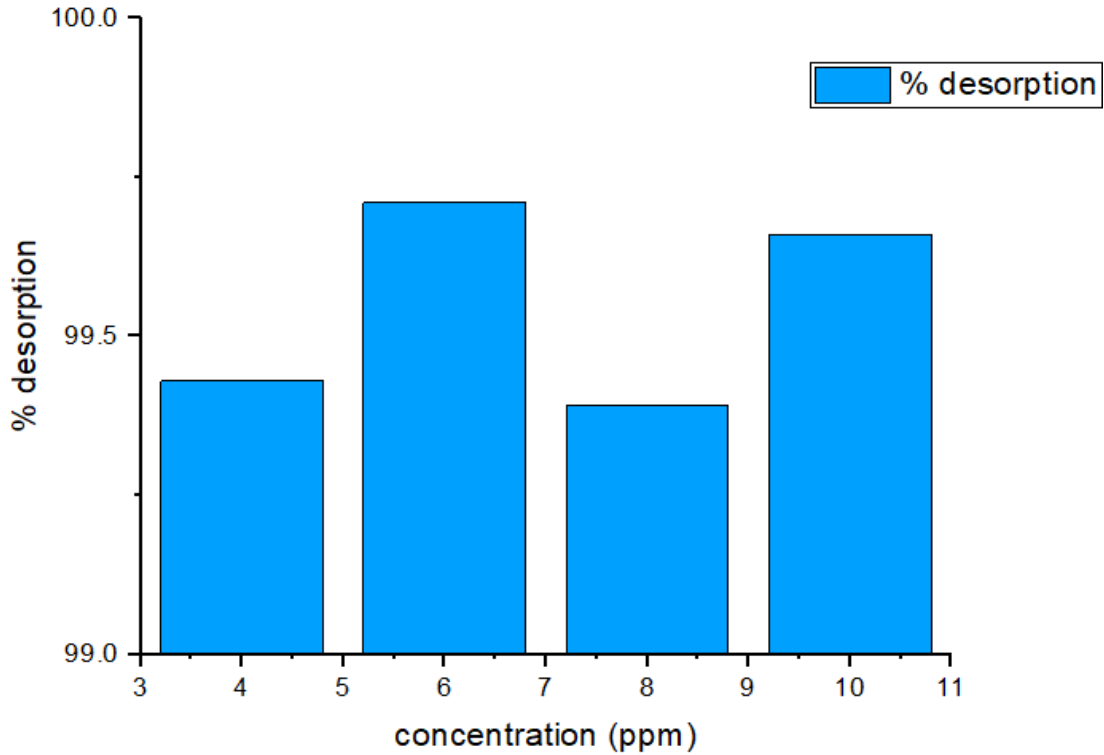


Figure 22: Percentage desorption of Cu (II) ions

The copper (II) ion desorption outcomes in this research show high desorption rates because the open surface of the composite contains oxygen-based functional groups for multi-directional metal ion absorption. Laboratory tests regarding zinc ions and magnetic carbon composites show that desorption efficiencies consistently stay above 98% indicating how surface composition affects material performance (Shahrashoub & Bakhtiari, 2021). In the process of metal desorption researchers can use pH controls along with acidic and saline solutions as eluents to reduce metal-adsorbent binding forces according to research performed on cadmium ion separation from polymer composites (Qi *et al.*, 2023). The composite material demonstrates strong abilities for ion-exchange and desorption making it suitable for water treatment operations that require efficient metal recovery along with multiple uses of the adsorbent.

4.8 Effects of Cations Interference on Adsorption of Cu (II) Ions

The selective behavior of MWCNTs/hydrochar of tea waste composite regarding copper (II) ion adsorption becomes evident through studies of simultaneous metal ion interferences (figure 23). The figure shows lead (Pb) along with copper (Cu) has minimal effect on copper ions adsorption efficiency as the sorption rate remains very

close to 100%. The strong affinity of the composite toward copper ions remains intact even when lead ions join the equilibrium. A remarkable relationship appears between copper ions and the functional groups on the composite surface because carboxyl, hydroxyl and aromatic π - π interactions create selective bonding locations (Gupta *et al.*, 2017).

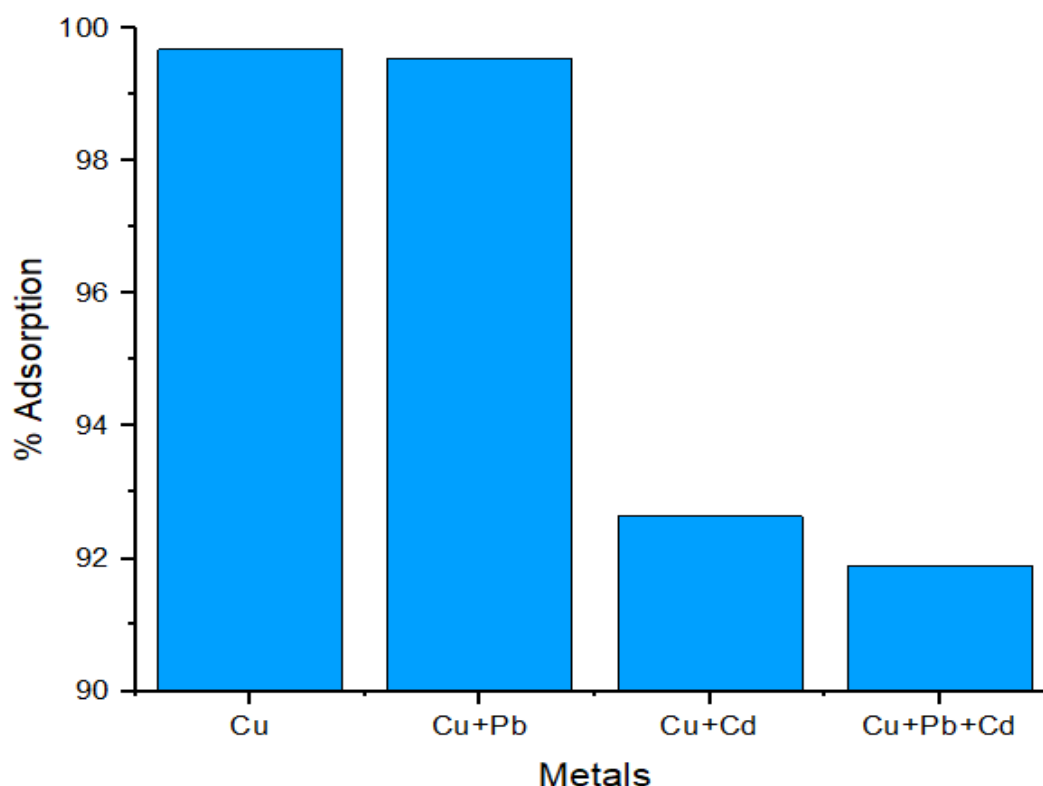


Figure 23: Cation interference on adsorption of Cu (II) ions

The adsorption efficiency for copper decreases noticeably when the adsorption system contains Cd and Cu together. The simultaneous presence of lead and cadmium ions (Cu+Pb+Cd) results in a further decrease of adsorption efficiency because cadmium ions compete very strongly for available sites. The identical properties of cadmium and copper ions with regard to ionic radii and charge results in cadmium out competing copper ions for active sites present on the adsorbent surface (Elboughdiri *et al.*, 2024). Wang *et al.* (2021), conducted studies that confirmed cadmium ions defeat copper ions for surface availability in carbon-based adsorbents since cadmium ions form stronger complexes with functional groups or exhibit superior mobility in the aqueous solution.

CHAPTER FIVE

SUMMARY, CONCLUSION AND RECOMMENDATIONS

5.1 Summary

Freshwater is of great importance for the continuation of life and for supporting important socio-economic functions like agriculture, manufacturing, and daily life use. Continued growth in urban, industrial, and agricultural activities has resulted in the release of heavy metals and other pollutants into natural water systems. Metals such as copper (Cu^{2+}), lead (Pb^{2+}), and cadmium (Cd^{2+}) are recognized as significant persistent pollutants causing major health problems for both people and water-based ecosystems. The presence of these metals in aquatic systems may cause human organs to be damaged, induce neurological problems, and increase cancer risks, and perturb ecosystem functions in water bodies.

Copper (II) ion pollution in River Kathita was selected as the primary focus in this study because of the river's importance to the regional community as a water source. The synthesis of a new, economically sustainable, and environmentally friendly adsorbent from multi-walled carbon nanotubes (MWCNTs) and tea waste hydrochar was intended to solve the problem of heavy metal contamination efficiently. The study further examined the physicochemical and biological quality of River Kathita at different times of the year and investigated how well, how often, and with what interferences the synthesized composite performs. The work provides important steps toward achieving improved water safety and encouraging the use of sustainable technologies, with a particular focus on underdeveloped areas.

5.1.1 Physicochemical Parameters

Seasonal changes, physicochemical characteristics of River Kathita were established during the dry season and wet season. The conductivity of the samples of the river differed throughout the dry season between 91.432–160.33 $\mu\text{S}/\text{cm}$, and between 2.120–9.398 NTU for turbidity. The pH ranged slightly acidic – neutral (6.4–7.3), the level of dissolved oxygen ranged between 4.053–4.890 mg/L, indicating moderate availability of oxygen. The temperature maintained within a small margin, between 24.033–24.3 °C. The nutrient analysis provided N concentration between 0.136 – 0.299 mg/L, with the concentration of the phosphorus being 0.025–0.04 mg/L. The total suspended solids

(TSS) were recorded to be 14 – 28.33 mg/L, with the total dissolved solids (TDS) ranging between 85-215 mg/L.

During the wet season, slightly lowered conductivity values (79.213–145.367 $\mu\text{S}/\text{cm}$) were measured, whereas turbidity largely increased (3.27–14.83 NTU). pH registered small changes to more neutral-alkaline (7.4 – 7.5) and the content of the dissolved oxygen largely increased (9.83 – 10.163 mg/L) which could be triggered by heightened mobility of the waters. The nitrogen content increased to 0.164–0.495 mg/L, whereas the content of the phosphorus increased to 0.066–0.081 mg/L. TSS increased to 36.667 – 53.33 to L. and TDS increased to 143.33 – 215 mg/L. The levels of the heavy metals also varied, Pb from 0.0119 to 0.0709 mg/L; Cu from 0.0080 to 0.7039 mg/L and Cd from 0.0525 to 0.0442 mg/L with heightened mobility during the wet season.

5.1.2 Biological Parameters

Biological river water quality was also established by sampling for total and faecal coliforms. The total coliform counts for the dry season were 18.667 – 207.667 mg/L while the faecal coliforms were 5.33 – 32.33 mg/L. These were already beyond proposed standards of safe recreational or agricultural use. For wet season, microbial contamination increased with the total coliform recorded between 18.33 to 1130 mg/L and the faecal coliform increasing between 11.33 to 86 mL. These were high figures showing extensive runoff as well as sewer discharge into the water during the rainy season, i.e., a high risk to the general public health to the communities reliant on this catchment for the source of water.

5.1.3 Adsorption Studies

The study combined a composite material prepared of multi-walled carbon nanotubes (MWCNTs) and hydrochar from tea waste to remove Cu^{2+} ions from water. FTIR and XRD profiles of the adsorbent represented the presence of functional groups such as $-\text{CH}_2$ and $=\text{C}-\text{H}$, necessary for metal ion bonding. Experiments on batch adsorption were carried out to determine the influence of: pH; contact time, initial metal concentration; temperature; speed and dosage of adsorbent, on the removal of copper. The results indicated that under optimum conditions the composite had a big removal efficiency of 96.5%. From the kinetic modeling, it was shown that the adsorption

process obeyed pseudo-second order reaction ($R^2 = 0.96683$) trend which implied the process being chemisorption driven. There was greater fit of the adsorption equilibrium data on Langmuir isotherm model ($R^2 = 0.87019$) indicating monolayer surface coverage of Cu^{2+} ions by homogenous surface.

5.1.4 Desorption studies

Desorption experiments were also used to determine the reusability of the prepared adsorbent. The findings showed high regeneration potential, with as high as 99% of the absorbed Cu^{2+} ions being efficiently desorbed. The MWCNTs/hydrochar composite is thus not only highly effective but also sustainable, given the fact that it can be recycled multiple times without the loss of functionality on a significant scale. The simplicity of regeneration further promotes its practicality within large-scale water treatment systems, leading to reduced costs as well as the preservation of the environment.

5.1.5 Interference Studies

Interference experiments were conducted to test the influence of other heavy metals, specifically Pb^{2+} and Cd^{2+} , on the Cu^{2+} ion adsorption. The addition of Pb^{2+} ions did not drastically influence the removal of Cu^{2+} , showing low competition for the adsorption sites. The addition of Cd^{2+} ions and the binary solution of Pb^{2+} and Cd^{2+} , however, caused a significant decrease in the efficiency of copper adsorption. The factor identified for this decrease included the occurrence of competitive interactions on the sorption sites, as well as disparities in the affinity for the active binding sites of the adsorbent material. The results, therefore, reinforce the consideration of multi-pollutant systems when developing solutions for treating polluted waters.

5.2 Conclusion

This experiment effectively proved the potential of a composite adsorbent composed of multi-walled carbon nanotubes and hydrochar of tea residue for the removal of copper ions from polluted river water. The resultant material showed high removal efficiency, desirable kinetic and equilibrium characteristics, and good regeneration capacity. River Kathita was confirmed to possess high levels of physicochemical and biological contaminants, especially during the wet season. Although the water stayed within acceptable limits for some parameters, the concentrations of the heavy metals, as well

as the load of microbes, were above the threshold of safety, highlighting the need for proper treatment measures urgently. Generally, the MWCNTs/hydrochar composite is a sustainable option for enhancing the quality of the polluted rivers' water.

5.3 Recommendations

Copper (Cu) is an essential trace element used in water systems for its antimicrobial properties and in plumbing materials such as pipes and fittings. In small amounts, copper supports metabolic processes in humans and aquatic organisms. However, excessive copper levels in water can be toxic. It may cause gastrointestinal irritation, liver and kidney damage, and neurological issues in humans. In aquatic environments, high copper concentrations can disrupt the growth, reproduction, and survival of fish and invertebrates. Prolonged exposure also leads to bioaccumulation, posing long-term ecological and health risks. It is recommended that:

- i. The MWCNTs/hydrochar composite be adopted for point-of-use water treatment, particularly in regions lacking centralized treatment infrastructure.
- ii. Continuous monitoring of River Kathita's water quality should be implemented to detect seasonal variations and address contamination risks promptly.
- iii. Public health interventions should focus on raising awareness about the impacts of untreated wastewater discharge and improper waste disposal. Integration of such eco-friendly materials into community-level water purification units can significantly reduce exposure to toxic heavy metals and waterborne pathogens.

5.4 Suggestions for Further Studies

Future work ought to focus on;

- i. The behavior of the MWCNTs/hydrochar composite in real-world settings, inclusive of continuous flow systems and a range of pollutant concentrations.
- ii. Studies should be conducted on the ability of the adsorbent to remove other prevalent pollutants, such as lead, cadmium, and pharmaceutical residues.
- iii. Extended monitoring of the composite's durability, adsorption efficiency across several uses, and economic viability are necessary for making the technology applicable at large scale.

REFERENCES

- Abila, R., Mutemi, M., Mutuku, E., Mutati, K., Mutinda, M., & Musyoka, C. M. (2012). Physico-chemical and bacteriological quality assessment of shallow wells in Kitui town, Kenya. MSc. thesis.
- Abiodun, O.-A. O., Oluwaseun, O., Oladayo, O. K., Abayomi, O., George, A. A., Opatola, E., Orah, R. F., Isukuru, E. J., Ede, I. C., & Oluwayomi, O. T. (2023). Remediation of heavy metals using biomass-based adsorbents: Adsorption kinetics and isotherm models. *Clean Technologies*, 5(3), 934–960.
- Achieng, A. O., Masese, F. O., Coffey, T. J., Raburu, P. O., Agembe, S. W., Febria, C. M., & Kaunda-Arara, B. (2021). Assessment of the ecological health of Afrotropical rivers using fish assemblages: A case study of selected rivers in the Lake Victoria Basin, Kenya. *Frontiers in Water*, 2, 620704.
- Achieng', A., Raburu, P., Kipkorir, E., Ngodhe, S., Obiero, K., & Ani-Sabwa, J. (2017). Assessment of water quality using multivariate techniques in River Sosiani, Kenya. *Environmental Monitoring and Assessment*, 189, 1–13.
- Adabi, S., Yazdanbakhsh, A., Shahsavani, A., Sheikhmohammadi, A., & Hadi, M. (2023). Removal of heavy metals from the aqueous solution by nanomaterials: A review with analysing and categorizing the studies. *Journal of Environmental Health Science and Engineering*, 21(2), 305–318.
- Adams, V. D. (2017). Water and wastewater examination manual (1st ed.). *Routledge*.
- Adesuyi, A. A., Ngwoke, M. O., Akinola, M. O., Njoku, K. L., & Jolaoso, A. O. (2016). Assessment of physicochemical characteristics of sediment from Nwaja Creek, Niger Delta, Nigeria. *Journal of Geoscience and Environment Protection*, 4(01), 16.
- Akubuenyi, F., Uttah, E., & Enyi-Idoh, K. (2013). Microbiological and physicochemical assessment of major sources of water for domestic uses in Calabar Metropolis Cross River state, Nigeria. *Transnational Journal of Science and Technology*, 3(2), 31–44.
- Al Sawaf, M. B., Kawanisi, K., & Bahreinimotlagh, M. (2024). Examining the relationship between rainfall, runoff, and turbidity during the rainy season in western Japan. *GeoHazards*, 5(1), 176–191.
- Aladese, M. A., & Pondei, J. O. (2021). Physicochemical and bacteriological properties of surface waters from two localities in rivers state, Nigeria. *Afr. J. Environ. Nat. Sci. Res*, 4(2), 39–58.
- Ali, R. M., Hamad, H. A., Hussein, M. M., & Malash, G. F. (2016). Potential of using green adsorbent of heavy metal removal from aqueous solutions: Adsorption kinetics, isotherm, thermodynamic, mechanism and economic analysis. *Ecological Engineering*, 91, 317–332.

- American Public Health Association, American Water Works Association, Water Pollution Control Federation, & Water Environment Federation. (1917). *Standard methods for the examination of water and wastewater* (Vol. 3). American Public Health Association.
- Ateş, A., Mert, Y., & Timko, M. T. (2023). Evaluation of characteristics of raw tea waste-derived adsorbents for removal of metals from aqueous medium. *Biomass Conversion and Biorefinery*, 1–16.
- Athulya, P., Sajeevan, A., Prasad, P. V., Sivalingam, R., & Sajeev, T. V. (2025). Diversity and distribution of aquatic insects and their relation to water quality parameters at the selected stations of the Chalakudy River, Kerala, India. *Aquatic Ecology*, 1–13.
- Atud, A. Q., Aghaindum, A. G., de Paul, Z. V., Buhnyuy, V. E., Nadège, A. T., & Bine, F. K. (2025). *Assessment of biological contamination and influence of physico-chemical factors of groundwater used for consumption in peri-urban areas of the Centre Region (Cameroon): Health risk associated with Microsporidia*.
- Aturamu, A. O. (2012). Physical, chemical and bacterial analyses of groundwater in Ikere township, southwestern Nigeria. *International Journal of Science and Technology*, 2(5), 301–308.
- Augustyn, Ł., Babula, A. M., Joniec, J., Stanek-Tarkowska, J., Hajduk, E., & Kaniuczak, J. (2016). Microbiological indicators of the quality of river water, used for drinking water supply. *Polish Journal of Environmental Studies*, 25(2), 511–519.
- Babalola, B. M., & Wilson, L. D. (2024). Valorization of Eggshell as Renewable Materials for Sustainable Biocomposite Adsorbents—An Overview. *Journal of Composites Science*, 8(10), 414.
- Balaram, V. (2020). Microwave plasma atomic emission spectrometry (MP-AES) and its applications—A critical review. *Microchemical Journal*, 159, 105483.
- Barakat, M. (2011). New trends in removing heavy metals from industrial wastewater. *Arabian Journal of Chemistry*, 4(4), 361–377.
- Bartram, J., Lewis, K., Lenton, R., & Wright, A. (2005). Focusing on improved water and sanitation for health. *The Lancet*, 365(9461), 810–812.
- Bayuo, J., Abukari, M. A., & Pelig-Ba, K. B. (2020). Desorption of chromium (VI) and lead (II) ions and regeneration of the exhausted adsorbent. *Applied Water Science*, 10(7), 171.
- Benrabah, S., Attoui, B., & Hannouche, M. (2016). Characterization of groundwater quality destined for drinking water supply of Khenchela City (eastern Algeria). *Journal of Water and Land Development*, 30(1), 13.

- Bhat, B., Parveen, S., & Hassan, T. (2018). Seasonal assessment of physicochemical parameters and evaluation of water quality of river Yamuna, India. *Advances in Environmental Technology*, 4(1), 41–49.
- Bhutia, D. (2024). Assessment of the health of streams of Sukhia Pokhari, Darjeeling (West Bengal) using Aquatic Macroinvertebrates. *Indian J. Applied & Pure Bio. Vol*, 39(2), 1157–1167.
- Bilal, A. (2022). *Biochar for adsorption remediation of Ciprofloxacin in wastewater*.
- BONARERI, S. P. (2013). *Effects of human activities on water quality of Rupingazi River, Embu County, Kenya*.
- Bora, M., & Goswami, D. C. (2017). Water quality assessment in terms of water quality index (WQI): Case study of the Kolong River, Assam, India. *Applied Water Science*, 7, 3125–3135.
- Borah, L., Senapati, K. K., Borgohain, C., Sarma, S., Roy, S., & Phukan, P. (2012). Preparation of ordered porous carbon from tea by chemical activation and its use in Cr (VI) adsorption. *Journal of Porous Materials*, 19, 767–774.
- Buridi, K. R., & Gedala, R. K. (2014). Study on determination of physicochemical parameters of groundwater in industrial area of pydibheemavaram, Vizianagaram District, Andhrapradesh, India. *Austin J Public Health Epidemiol*, 1(2), 1–2.
- Cassardo, C., & Jones, J. A. A. (2011). Managing water in a changing world. *Water*, 3(2), 618–628.
- Chebet, E. B., Kibet, J. K., & Mbui, D. (2020). The assessment of water quality in river Molo water basin, Kenya. *Applied Water Science*, 10, 1–10.
- Chen, C.-F., Ju, Y.-R., Chen, C.-W., & Dong, C.-D. (2016). Vertical profile, contamination assessment, and source apportionment of heavy metals in sediment cores of Kaohsiung Harbor, Taiwan. *Chemosphere*, 165, 67–79.
- Cheng, X., Zhong, J., Meng, J., Yang, M., Jia, F., Xu, Z., Kong, H., & Xu, H. (2011). Characterization of multiwalled carbon nanotubes dispersing in water and association with biological effects. *Journal of Nanomaterials*, 2011(1), 938491.
- Christine, A. A., Kibet, J. K., Kiprop, A. K., & Were, M. L. (2018). The assessment of bore-hole water quality of Kakamega County, Kenya. *Applied Water Science*, 8, 1–8.
- Chukwu Okeah, G., Ezekwe, I., & Nigeria, P. H. (n.d.). *Seasonal Variation in Surface and Groundwater Quality in an Oil-Polluted Environment of the Niger Delta*.
- Cotruvo, J. A. (2017). 2017 WHO guidelines for drinking water quality: First addendum to the fourth edition. *Journal-American Water Works Association*, 109(7), 44–51.

- Cronk, J. K., & Fennessy, M. S. (2016). *Wetland plants: Biology and ecology*. CRC press.
- Cukierman, A. L., Nunell, G. V., & Bonelli, P. R. (2019). Removal of emerging pollutants from water through adsorption onto carbon-based materials. In *Emerging and nanomaterial contaminants in wastewater* (pp. 159–213). Elsevier.
- Darwall, W., Bremerich, V., De Wever, A., Dell, A. I., Freyhof, J., Gessner, M. O., Grossart, H., Harrison, I., Irvine, K., & Jähnig, S. C. (2018). The Alliance for Freshwater Life: A global call to unite efforts for freshwater biodiversity science and conservation. *Aquatic Conservation: Marine and Freshwater Ecosystems*, 28(4), 1015–1022.
- Davidkova, D. F., Graham, M. C., MacLeod, D., Romero-Vargas Castrillón, S., & Correia Semiao, A. J. (2024). Analysis of Tubular NF Plants in Scotland Indicates That Summer Temperatures and Redox-Sensitive Elements Are Correlated with Membrane Biofouling and Shortened Useful Life. *ACS Es&t Water*, 4(11), 5002–5012.
- Dehghani Ahmadabadi, M., Mirzaei, F., & Saedi, M. (2024). Investigating the seasonal changes in the chemical and microbial quality of water in the transmission channel of the Faculty of Agriculture and Natural Resources of Tehran University. *Irrigation and Water Engineering*, 14(3), 96–108.
- Dey, S., Haripavan, N., Basha, S., & Babu, G. (2021). Removal of ammonia and nitrates from contaminated water by using solid waste bio-adsorbents. *Current Research in Chemical Biology*, 1, 100005.
- Dichiara, A. B., Webber, M. R., Gorman, W. R., & Rogers, R. E. (2015). Removal of copper ions from aqueous solutions via adsorption on carbon nanocomposites. *ACS Applied Materials & Interfaces*, 7(28), 15674–15680.
- dos Santos, A. M., Dantas Filho, J. V., Hurtado, F. B., da Silva, F. C., Teixeira, N. R., de Arruda Silva, S. M., de Oliveira, R. F., & Pontuschka, R. B. (2025). Sanitary aspects, evidence of microplastics and seasonality interference in freshwater from shallow wells in Presidente Médici city-Rondonia state, Brazil. *OBSERVATÓRIO DE LA ECONOMÍA LATINOAMERICANA*, 23(1), e8640–e8640.
- Duan, C., Ma, T., Wang, J., & Zhou, Y. (2020). Removal of heavy metals from aqueous solution using carbon-based adsorbents: A review. *Journal of Water Process Engineering*, 37, 101339.
- Dugan, I., Pereira, P., Kisic, I., & Bogunovic, I. (2024). Temporal dynamics of Soil Erosion and nutrient loss in Croatian Orchard: Experimental insights into resilience mechanisms. *Environmental Processes*, 11(4), 53.

- Dwivedi, a., & Rajput, d. p. s. (2014). studies on adsorptive removal of heavy metal (cu, cd) from aqueous solution by tea waste adsorbent. *Journal of Industrial Pollution Control*, 30(1).
- Eatemadi, A., Daraee, H., Karimkhanloo, H., Kouhi, M., Zarghami, N., Akbarzadeh, A., Abasi, M., Hanifehpour, Y., & Joo, S. W. (2014). Carbon nanotubes: Properties, synthesis, purification, and medical applications. *Nanoscale Research Letters*, 9, 1–13.
- El Naeem, G. A., Abd-Elhamid, A., Farahat, O. O., El-Bardan, A. A., Soliman, H. M., & Nayl, A. (2022). Adsorption of crystal violet and methylene blue dyes using a cellulose-based adsorbent from sugarcane bagasse: Characterization, kinetic and isotherm studies. *Journal of Materials Research and Technology*, 19, 3241–3254.
- Elboughdiri, N., Ferkous, H., Rouibah, K., Boublija, A., Delimi, A., Yadav, K. K., Erto, A., Ghernaout, D., Salih, A. A., & Benaissa, M. (2024). Comprehensive investigation of Cu²⁺ adsorption from wastewater using olive-waste-derived adsorbents: Experimental and molecular insights. *International Journal of Molecular Sciences*, 25(2), 1028.
- EPA, U. (2014). *Cyanobacteria and cyanotoxins: Information for drinking water systems*.
- Ewis, D., & Hameed, B. (2021). A review on microwave-assisted synthesis of adsorbents and its application in the removal of water pollutants. *Journal of Water Process Engineering*, 41, 102006.
- Fahad, S. A., Nawab, M. S., Shaida, M. A., Verma, S., Khan, M. U., Siddiqui, V., Naushad, M., Saleem, L., & Farooqi, I. H. (2023). Carbon based adsorbents for the removal of U (VI) from aqueous medium: A state of the art review. *Journal of Water Process Engineering*, 52, 103458.
- Fei, Y., & Hu, Y. H. (2022). Design, synthesis, and performance of adsorbents for heavy metal removal from wastewater: A review. *Journal of Materials Chemistry A*, 10(3), 1047–1085.
- Fouad, M. S., Mustafa, E. F., Hellal, M. S., & Mwaheb, M. A. (2024). A comprehensive assessment of water quality in Fayoum depression, Egypt: Identifying contaminants, antibiotic pollution, and adsorption treatability study for remediation. *Scientific Reports*, 14(1), 18849.
- Fu, F., & Wang, Q. (2011). Removal of heavy metal ions from wastewaters: A review. *Journal of Environmental Management*, 92(3), 407–418.
- Gajek, R., Barley, F., & She, J. (2013). Determination of essential and toxic metals in blood by ICP-MS with calibration in synthetic matrix. *Analytical Methods*, 5(9), 2193–2202.

- Gebre, A., Demissie, H., Mengesha, S., & Segni, M. (2016). The pollution profile of Modjo River due to industrial wastewater discharge. *Modjo Town, Oromia, Ethiopia. Journal of Environmental & Analytical Toxicology*, 6, 363.
- Gemmell, M. E., & Schmidt, S. (2013). Is the microbiological quality of the Msunduzi River (KwaZulu-Natal, South Africa) suitable for domestic, recreational, and agricultural purposes? *Environmental Science and Pollution Research*, 20, 6551–6562.
- Gichuki, J., & Gichumbi, J. (2012). Physico-chemical analysis of ground water from Kihara Division, Kiambu County, Kenya. *Journal of Chemical, Biological and Physical Sciences (JCBPS)*, 2(4), 2193.
- Githinji, P. M. (2019). *Surface Water Quality Assessment in Ng'ethu Water Works, Chania Catchment, Kenya*.
- Gitonga, r. d. (2021). *assessment of ecosystem integrity based on habitat quality and fish indices of river Kathita and associated dams in upper tana basin, Kenya..*
- Gopalkrushna, H. M. (2011). *Determination of physico-chemical parameters of surface water samples in and around Akot city*.
- Gupta, V. K., Agarwal, S., Bharti, A. K., & Sadegh, H. (2017). Adsorption mechanism of functionalized multi-walled carbon nanotubes for advanced Cu (II) removal. *Journal of Molecular Liquids*, 230, 667–673.
- Gupta, V. K., Nayak, A., Bhushan, B., & Agarwal, S. (2015). A critical analysis on the efficiency of activated carbons from low-cost precursors for heavy metals remediation. *Critical Reviews in Environmental Science and Technology*, 45(6), 613–668.
- Hasanuzzaman, M., Hakim, K., Nahar, K., & Alharby, H. F. (2019). Plant abiotic stress tolerance. *Bhuyan, MHMB, Hasanuzzaman, M., Nahar, K., Mahmud, JA, Parvin, K., Bhuiyan, TF, Fujita, M.*
- Hashmi, M. Z., Yu, C., Shen, H., Duan, D., Shen, C., Lou, L., & Chen, Y. (2014). Concentrations and Human Health Risk Assessment of Selected Heavy Metals in Surface Water of the Siling Reservoir Watershed in Zhejiang Province, China. *Polish Journal of Environmental Studies*, 23(3).
- Hayat, K., Iqbal, H., Malik, U., Bilal, U., & Mushtaq, S. (2015). Tea and its consumption: Benefits and risks. *Critical Reviews in Food Science and Nutrition*, 55(7), 939–954.
- Hussain, A., Madan, S., & Madan, R. (2021). Removal of heavy metals from wastewater by adsorption. *Heavy Metals—Their Environmental Impacts and Mitigation*.
- Hussain, S., Anjali, K., Hassan, S. T., & Dwivedi, P. B. (2018). Waste tea as a novel adsorbent: A review. *Applied Water Science*, 8, 1–16.

- Ibrahim, A. (2025). The physicochemical water pollution of River Ginzo's seasonal variations For Irrigation, Katsina Metropolis, Katsina State, Nigeria. *International Journal of African Development and Sustainable Research*.
- Ibrahim, B., Auta, J., & Balogun, J. (2009). An assessment of the physico-chemical parameters of Kontagora Reservoir, Niger State, Nigeria. *Bayero Journal of Pure and Applied Sciences*, 2(1), 64–69.
- Ighalo, J. O., Rangabhashiyam, S., Dulta, K., Umeh, C. T., Iwuozor, K. O., Aniagor, C. O., Eshiemogie, S. O., Iwuchukwu, F. U., & Igwegbe, C. A. (2022). Recent advances in hydrochar application for the adsorptive removal of wastewater pollutants. *Chemical Engineering Research and Design*, 184, 419–456.
- Ikhsani, I. Y., Wong, K. H., Kim, T., Mashio, A. S., Norisuye, K., & Obata, H. (2024). Biogeochemistry of dissolved trace metals in the Bay of Bengal. *Marine Chemistry*, 262, 104394.
- Inglezakis, V., Pouloupoulos, S., Arkhangelsky, E., Zorpas, A., & Menegaki, A. (2016). Aquatic environment. In *Environment and development* (pp. 137–212). Elsevier.
- Islam, M., Ekhwan, T., Rasli, F., & Goh, C. (2024). Assessment of Physicochemical Properties of Water and Public Perceptions of Water Quality in Tasik Chini, Pahang, Malaysia. *Nature Environment and Pollution Technology*, 23(4), 2179–2188.
- Jain, S., & Agarwal, M. (2012). Study on physico-chemical characteristics of ground water of various villages around Raisar. *Journal of Chemical, Biological and Physical Sciences (JCBPS)*, 2(3), 1551.
- Joseph, L., Jun, B.-M., Flora, J. R., Park, C. M., & Yoon, Y. (2019). Removal of heavy metals from water sources in the developing world using low-cost materials: A review. *Chemosphere*, 229, 142–159.
- Juneja, T., & Chaudhary, A. (2013). Assessment of water quality and its effects on the health of residents of Jhunjhunu district, Rajasthan: A cross sectional study. *Journal of Public Health and Epidemiology*, 5(4), 186–191.
- Kambo, H. S., & Dutta, A. (2015). A comparative review of biochar and hydrochar in terms of production, physico-chemical properties and applications. *Renewable and Sustainable Energy Reviews*, 45, 359–378.
- Katsou, E., Malamis, S., Tzanoudaki, M., Haralambous, K. J., & Loizidou, M. (2011). Regeneration of natural zeolite polluted by lead and zinc in wastewater treatment systems. *Journal of Hazardous Materials*, 189(3), 773–786.

- Khanzada, A. K., Al-Hazmi, H. E., Kurniawan, T. A., Majtacz, J., Piechota, G., Kumar, G., Ezzati, P., Saeb, M. R., Rabiee, N., & Karimi-Maleh, H. (2024). Hydrochars as a bio-based adsorbent for heavy metals removal: A review of production processes, adsorption mechanisms, kinetic models, regeneration and reusability of hydrochar. *Science of the Total Environment*, 173972.
- Khounda, N., Phukonb, P., & Bhattacharyyaa, K. (2012). *Physico-chemical studies on surface water quality in the Jia-Bharali river basin, North Brahmaputra plain, India*.
- Khulbe, K., & Matsuura, T. (2018). Removal of heavy metals and pollutants by membrane adsorption techniques. *Applied Water Science*, 8, 1–30.
- Kızıldaş, H. (2024). Production of highly effective adsorbent from tea waste, and its adsorption behaviors and characteristics for the removal of Rhodamine B. *International Journal of Environmental Analytical Chemistry*, 104(8), 1730–1749.
- Kodavanti, P. R. S., & Loganathan, B. G. (2017). Organohalogen pollutants and human health. *The International Encyclopedia of Public Health*. Eds. SR Quah, WC Cockerham, 5, 359–366.
- Kołodziejńska, D., Krukowska, J., & Thomas, P. (2017). Comparison of sorption and desorption studies of heavy metal ions from biochar and commercial active carbon. *Chemical Engineering Journal*, 307, 353–363.
- Kudryavtseva, V., Popova, T., & Shigaeva, T. (2024). Influence of Seasonal and Anthropogenic Factors on Changes in Concentrations of Heavy Metals in Urban Water Systems. *Russian Journal of General Chemistry*, 94(13), 3602–3610.
- Kumar, S. (2023). Carbon based nanomaterial for removal of heavy metals from wastewater: A review. *International Journal of Environmental Analytical Chemistry*, 103(19), 7961–7978.
- Kumkum, P., & Kumar, S. (2024). A review on biochar as an adsorbent for Pb (II) removal from water. *Biomass*, 4(2), 243–272.
- Kundu, S., Sadeque, A. N., & Jubaer, S. (n.d.). *The Crucial Role of Sediment Excavation in Safeguarding Haor Area Ecosystems of Bangladesh*.
- Kurniawan, T. A., Chan, G. Y., Lo, W.-H., & Babel, S. (2006). Physico-chemical treatment techniques for wastewater laden with heavy metals. *Chemical Engineering Journal*, 118(1–2), 83–98.
- Kwon, T.-N., & Jeon, C. (2012). Desorption and regeneration characteristics for previously adsorbed indium ions to phosphorylated sawdust. *Environmental Engineering Research*, 17(2), 65–67.

- Lata, S., Singh, P., & Samadder, S. (2015). Regeneration of adsorbents and recovery of heavy metals: A review. *International Journal of Environmental Science and Technology*, *12*, 1461–1478.
- Lee, J., Perera, D., Glickman, T., & Taing, L. (2020). Water-related disasters and their health impacts: A global review. *Progress in Disaster Science*, *8*, 100123.
- Lei, Y., Su, H., & Tian, F. (2018). A novel nitrogen enriched hydrochar adsorbents derived from salix biomass for Cr (VI) adsorption. *Scientific Reports*, *8*(1), 4040.
- Li, J., Chen, S., Sheng, G., Hu, J., Tan, X., & Wang, X. (2011). Effect of surfactants on Pb (II) adsorption from aqueous solutions using oxidized multiwall carbon nanotubes. *Chemical Engineering Journal*, *166*(2), 551–558.
- Li, P., & Wu, J. (2019). Drinking water quality and public health. *Exposure and Health*, *11*(2), 73–79.
- Lightman, S. A., & Moyo, S. (2024). Lead levels and abundance of microplastics in surface water and sediment along a rural–urban river gradient. *Discover Water*, *4*(1), 93.
- Likambo, W. (2014). *Assessment of borehole water quality and consumption in Yei County South Sudan*.
- Lintern, A., Webb, J., Ryu, D., Liu, S., Bende-Michl, U., Waters, D., Leahy, P., Wilson, P., & Western, A. (2018). Key factors influencing differences in stream water quality across space. *Wiley Interdisciplinary Reviews: Water*, *5*(1), e1260.
- Liu, H., Meng, Q., Zhao, X., Ye, Y., & Tong, H. (2021). Inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectrometer (ICP-OES)-based discrimination for the authentication of tea. *Food Control*, *123*, 107735.
- Liu, M., Zhao, L., Lin, L., Zhang, Y., Huang, H., Deng, W., He, Y., Tao, J., Hu, Y., & Nan, L. (2024). Distribution characteristics, sources and risk assessment of heavy metals in the surface sediments from the largest tributary of the Lancang River in the Tibet Plateau, China. *Environmental Geochemistry and Health*, *46*(10), 414.
- Malik, D., Jain, C., Yadav, A. K., & Vishwavidyalaya, G. K. (2015). Preparation and characterization of plant based low cost adsorbents. *Journal of Global Biosciences*, *4*(1), 1824–1829.
- Mamawal, D. R. D., & Rivera, W. L. (2025). Combined application of metagenomics and FEAST to trace sources of microbial eukaryotic contamination in the Pasig–Marikina–San Juan (PAMARISAN) river system in Metro Manila, Philippines. *Environmental Monitoring and Assessment*, *197*(2), 196.

- Mathew, S., Mathur, D., Chang, A. B., McDonald, E., Singh, G. R., Nur, D., & Gerritsen, R. (2017). Examining the effects of ambient temperature on pre-term birth in Central Australia. *International Journal of Environmental Research and Public Health*, *14*(2), 147.
- Mbura, K. S. (2018a). Assessment of selected physico-chemical parameters of ground water in Tharaka Nithi County, Kenya. *Masters Degree Thesis. Kenyatta University, Kenya*.
- Mbura, K. S. (2018b). Assessment of selected physico-chemical parameters of ground water in Tharaka Nithi County, Kenya. *Masters Degree Thesis. Kenyatta University, Kenya*.
- Mgbemena, I., Okechukwu, I., Onyemekara, N., & Nnokwe, J. (2012). *Physicochemical and microbial characterization of Somberiro River in Ahoada east local government area, Rivers State, Nigeria*.
- Mishra, S. (2014). Adsorption–desorption of heavy metal ions. *Current Science*, 601–612.
- Mitova, R. (2025). Hiking trail impacts on eutrophication of the Seven Rila Lakes, Rila National Park, Bulgaria. *One Ecosystem*, *10*, e139690.
- Mohiuddin, M., Hossain, M. B., Ali, M. M., Hossain, M. K., Habib, A., Semme, S. A., Rakib, M. R. J., Rahman, M. A., Yu, J., & Al-Sadoon, M. K. (2022). Human health risk assessment for exposure to heavy metals in finfish and shellfish from a tropical estuary. *Journal of King Saud University-Science*, *34*(4), 102035.
- Moreno-Bermedo, L., Correa-Puerta, J., González-Fuentes, C., Escalona, N., Onfray, C., & Thiam, A. (2025). Tea Waste as a Sustainable Catalyst Support for Enhanced Removal of Contaminants of Emerging Concern via the Electro-Fenton Process: A Circular Economy Approach. *Applied Sciences*, *15*(3), 1418.
- Mubarak, N. M., Sahu, J. N., Abdullah, E. C., & Jayakumar, N. S. (2016). Rapid adsorption of toxic Pb (II) ions from aqueous solution using multiwall carbon nanotubes synthesized by microwave chemical vapor deposition technique. *Journal of Environmental Sciences*, *45*, 143–155.
- Mudhafar, M., Zainol, I., Aiza Jaafar, C., Alsailawi, H., & Majhool, A. A. (2020). Two green synthesis methods to prepared nanoparticles of Ag: Two sizes and shapes via using extract of *M. dubia* leaves. *Journal of Computational and Theoretical Nanoscience*, *17*(7), 2882–2889.
- Mukhwana, A. (2019). *Evaluating the Effectiveness of Waste Management Systems for Tea Factory in Kenya: A Case Study of Maramba Tea Factory in Kiambu County*.
- Muriithi, F. K., & Yu, D. (2015). Understanding the impact of intensive horticulture land-use practices on surface water quality in Central Kenya. *Environments*, *2*(4), 521–545.

- Musarurwa, H., & Tavengwa, N. T. (2020). Application of carboxymethyl polysaccharides as bio-sorbents for the sequestration of heavy metals in aquatic environments. *Carbohydrate Polymers*, 237, 116142.
- Nandal, M., Hooda, R., & Dhania, G. (2014). Tea wastes as a sorbent for removal of heavy metals from wastewater. *Int. J. Curr. Eng. Technol*, 4(1), 244–247.
- Nekouei, F., & Nekouei, S. (2014). Determination of copper, nickel and cobalt in water and food samples by FAAS after separation and preconcentration using multi walled carbon nanotubes modified by methyl-(2-pyridyl) ketone oxime. *Indian J. Sci. Res*, 8(1), 138–145.
- Nieder, R., Benbi, D. K., Reichl, F. X., Nieder, R., Benbi, D. K., & Reichl, F. X. (2018). Reactive water-soluble forms of nitrogen and phosphorus and their impacts on environment and human health. *Soil Components and Human Health*, 223–255.
- Njuguna, S. M., Yan, X., Gituru, R. W., Wang, Q., & Wang, J. (2017). Assessment of macrophyte, heavy metal, and nutrient concentrations in the water of the Nairobi River, Kenya. *Environmental Monitoring and Assessment*, 189, 1–14.
- Nyongesa, D. S., Lung'ayia, H., & Shivoga, W. A. (2016). Differences in water quality in relation to human activities along River Shimiche ecosystem, Western Kenya. *International Journal of Scientific Research in Science, Engineering and Technology*, 2, 786–796.
- Obada, M. C. C., Oliveira, M. E. F. Z., Elguera, N. Y. M., Pulcha, S. E. S., Banda, A. A. P., Ortiz, J. A. Q., Murillo, V. S., & Pacheco, H. G. J. (2025). Assessment of heavy metal contamination in surface sediments: Seasonal influence in the Majes-Camaná basin of the Arequipa region, Peru. *Results in Engineering*, 25, 103673.
- Ochiba, N., Abong'o, D., & Onyatta, J. (2021). *The Assessment of The Effect of Proximity of Septic Tanks on The Levels of Selected Heavy Metals in Borehole Water from Ongata Rongai, Kajiado County, Kenya*.
- O'connell, M. J. (2018). *Carbon nanotubes: Properties and applications*. CRC press.
- Odada, E. O., Olago, D. O., Bugenyi, F., Kulindwa, K., Karimumuryango, J., West, K., Ntiba, M., Wandiga, S., Aloo-Obudho, P., & Achola, P. (2003). Environmental assessment of the east African rift valley lakes. *Aquatic Sciences*, 65, 254–271.
- Ombaka, O., & Gichumbi, J. (2012). Water quality assessment of Ruguti river in Meru South, Kenya. *Int J Water Resour Environ Eng*, 4(12), 404–414.
- Ombaka, O., Gichumbi, J., & Kibara, D. (2013a). Evaluation of ground water and tap water quality in the villages surrounding Chuka town, Kenya. *Journal of Chemical, Biological and Physical Sciences (JCBPS)*, 3(2), 1551.

- Ombaka, O., Gichumbi, J., & Kibara, D. (2013b). Evaluation of ground water and tap water quality in the villages surrounding Chuka town, Kenya. *Journal of Chemical, Biological and Physical Sciences (JCBPS)*, 3(2), 1551.
- Ombaka, O., Gichumbi, J., & Kinyua, C. (2012). Status of Water Quality of Naka River in Meru South, Kenya. *International Journal of Modern Chemistry*, 3(1), 23–38.
- Omri, A., & Benzina, M. (2012). Characterization of activated carbon prepared from a new raw lignocellulosic material: Ziziphus spina-christi seeds. *Journal de La Société Chimique de Tunisie*, 14, 175–183.
- Orina, E., Getabu, A., Omondi, R., & Emmy, S. (2017). Ecosystem integrity of River Kuja based on habitat and fish biotic indices. *International Journal of Tropical Hydrobiology and Fisheries*, 1, 7–13.
- Otieno, F. A. O., Olumuyiwa, I. O., & Ochieng, G. M. (2012). Groundwater: Characteristics, qualities, pollutions and treatments: An overview. *African Journal of Agricultural Research*.
- OTIENO, O. S. (2015). *Physico-chemical and bacteriological quality of water from five rural catchment areas of Lake Victoria basin in Kenya*.
- Owhonka, A., Fubara, E. F., & Justice, O. B. (2021). Wastewater quality-It's impact on the environment and human physiology: A review. *Int. J. Adv. Res. Innov*, 9, 43–58.
- Pandey, G., & Madhuri, S. (2014). Heavy metals causing toxicity in animals and fishes. *Research Journal of Animal, Veterinary and Fishery Sciences*, 2(2), 17–23.
- Paneque, M., De la Rosa, J., Kern, J., Reza, M., & Knicker, H. (2017). Hydrothermal carbonization and pyrolysis of sewage sludges: What happen to carbon and nitrogen? *Journal of Analytical and Applied Pyrolysis*, 128, 314–323.
- Petersen, J., & McLaughlin, S. (2016). *Laboratory exercises in microbiology: Discovering the unseen world through hands-on investigation*.
- Petrella, A., Petrella, M., Boghetich, G., Basile, T., Petruzzelli, V., & Petruzzelli, D. (2012). Heavy metals retention on recycled waste glass from solid wastes sorting operations: A comparative study among different metal species. *Industrial & Engineering Chemistry Research*, 51(1), 119–125.
- Planeta, K., Kubala-Kukus, A., Drozd, A., Matusiak, K., Setkowicz, Z., & Chwiej, J. (2021). The assessment of the usability of selected instrumental techniques for the elemental analysis of biomedical samples. *Scientific Reports*, 11(1), 3704.
- Pohl, A. (2020). Removal of heavy metal ions from water and wastewaters by sulfur-containing precipitation agents. *Water, Air, & Soil Pollution*, 231(10), 503.

- Pontoni, L. (2016). *Accumulation and colloidal mobilization of trace heavy metals in soil irrigated with treated wastewater*.
- Poonam, T., Tanushree, B., & Sukalyan, C. (2013). Water quality indices-important tools for water quality assessment: A review. *International Journal of Advances in Chemistry*, 1(1), 15–28.
- Prüss-Üstün, A., Wolf, J., Corvalán, C., Bos, R., & Neira, M. (2016). *Preventing disease through healthy environments: A global assessment of the burden of disease from environmental risks*. World Health Organization.
- Qasem, N. 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.
- Qhanavati, L., Hekmati, A. H., Rashidi, A., & Shafiekhani, A. (2021). Optimization of the process of removal of acidic blue dye-74 from textile wastewater with modified nanozeolite. *Journal of Quality Engineering and Management*, 11(2), 155–176.
- Qi, D., Zhang, H., Zhou, Z., & Ren, Z. (2023). Cadmium ion-imprinted polymers for adsorption and detection of cadmium ions. *Journal of Environmental Chemical Engineering*, 11(5), 110804.
- Qin, Y., Alam, A. U., Pan, S., Howlader, M. M., Ghosh, R., Hu, N.-X., Jin, H., Dong, S., Chen, C.-H., & Deen, M. J. (2018). Integrated water quality monitoring system with pH, free chlorine, and temperature sensors. *Sensors and Actuators B: Chemical*, 255, 781–790.
- Raji, Z., Karim, A., Karam, A., & Khalloufi, S. (2023). *Adsorption of heavy metals: Mechanisms, kinetics, and applications of various adsorbents in wastewater remediation—A review*. 1(3), 775–805.
- Rajiv, P., Hasna, A., Kamaraj, M., Rajeshwari, S., & Sankar, A. (2012). Physico chemical and microbial analysis of different river waters in western Tamil Nadu, India. *Research Journal of Environment Sciences*, 1(1), 2–6.
- Rashed, M. N., Gad, A., & AbdEldaiem, A. (2019). Novel Composite from Glass Waste and Activated Carbon for Heavy Metals Removal from Well Water in Semi-arid Regions. *International Journal of Water Resources and Arid Environments*, 8(1), 39–48.
- Rashko, M. N., Hamad, S. M., Barzinjy, A. A., & Hamad, A. H. (2022). Mechanical properties of carbon nanotubes (CNTs): A review. *Eurasian Journal of Science and Engineering*, 8(2), 54–68.
- Recha, C. W., Makokha, G. L., & Shisanya, C. A. (2017). Climate variability and causes: From the perspective of the Tharaka people of eastern Kenya. *Geoscience Letters*, 4, 1–8.

- Revellame, E. D., Fortela, D. L., Sharp, W., Hernandez, R., & Zappi, M. E. (2020). Adsorption kinetic modeling using pseudo-first order and pseudo-second order rate laws: A review. *Cleaner Engineering and Technology*, *1*, 100032.
- Rezania, S., Darajeh, N., Rupani, P. F., Mojiri, A., Kamyab, H., & Taghavijeloudar, M. (2024). Recent advances in the adsorption of different pollutants from wastewater using carbon-based and metal-oxide nanoparticles. *Applied Sciences*, *14*(24), 11492.
- Rice, E. W., Baird, R. B., Eaton, A. D., & Clesceri, L. S. (2012). *Standard methods for the examination of water and wastewater*.
- Rodrigues, C., & Cunha, M. Â. (2017). Assessment of the microbiological quality of recreational waters: Indicators and methods. *Euro-Mediterranean Journal for Environmental Integration*, *2*, 1–18.
- Rodríguez, C., Briano, S., & Leiva, E. (2020). Increased adsorption of heavy metal ions in multi-walled carbon nanotubes with improved dispersion stability. *Molecules*, *25*(14), 3106.
- Saad, A. B., M'barek, N. B., Boughalmi, S., & M'barek-Jemai, M. B. (2025). Impact of a lagoon with high anthropic activity on a World Heritage Site. *Environmental Monitoring and Assessment*, *197*(2), 1–20.
- Sabino, H., Júnior, G. C. S., & Menezes, J. (2024). Seasonal spatial distribution of groundwater suitability in the Cabo Frio shallow coastal aquifer, Rio de Janeiro, Brazil: Applying groundwater quality index and GIS approaches. *Sustainable Water Resources Management*, *10*(6), 1–15.
- Salam, M. A., Al-Zhrani, G., & Kosa, S. A. (2012). Simultaneous removal of copper (II), lead (II), zinc (II) and cadmium (II) from aqueous solutions by multi-walled carbon nanotubes. *Comptes Rendus Chimie*, *15*(5), 398–408.
- Saputra, N. A., Syafii, W., Pari, G., Nawawi, D. S., & Maddu, A. (2023). Preparation and application of a novel adsorbent from red calliandra hydrochar for pollutant remediation. *South African Journal of Chemical Engineering*, *46*, 351–360.
- Sarda, P., & Sadgir, P. (2015). Assessment of multi parameters of water quality in surface water bodies-a review. *Int J Res Appl Sci Eng Technol*, *3*(8), 331–336.
- Sellami, M., Riahi, H., Maatallah, K., Ferjani, H., Bouaziz, M. C., & Ladeb, M. F. (2020). Skeletal fluorosis: Don't miss the diagnosis! *Skeletal Radiology*, *49*, 345–357.
- Sevilla, M., Carro-Rodríguez, J., Díez, N., & Fuertes, A. B. (2020). Straightforward synthesis of Sulfur/N, S-codoped carbon cathodes for Lithium-Sulfur batteries. *Scientific Reports*, *10*(1), 4866.
- Sewe, H. A. (2013). *A study on the Efficiency of Dandora Domestic and Industrial Wastewater Treatment Plant in Nairobi*.

- Shahrashoub, M., & Bakhtiari, S. (2021). The efficiency of activated carbon/magnetite nanoparticles composites in copper removal: Industrial waste recovery, green synthesis, characterization, and adsorption-desorption studies. *Microporous and Mesoporous Materials*, 311, 110692.
- Sheraz, N., Shah, A., Haleem, A., & Iftikhar, F. J. (2024). Comprehensive assessment of carbon-, biomaterial- and inorganic-based adsorbents for the removal of the most hazardous heavy metal ions from wastewater. *RSC Advances*, 14(16), 11284–11310.
- Shi, Y., Li, H., Rong, Y., Bai, L., Chi, M., Xu, X., Li, C., Bai, H., & Liu, Y. (2022). The improving of Cd²⁺ adsorption performance of hydrochar obtained from corn straw waste with KOH activation. *Water, Air, & Soil Pollution*, 233(12), 502.
- Shmeis, R. M. A. (2018). Water chemistry and microbiology. In *Comprehensive analytical chemistry* (Vol. 81, pp. 1–56). Elsevier.
- Shruthi, M., & Anil, N. (2018). A comparative study of dental fluorosis and non-skeletal manifestations of fluorosis in areas with different water fluoride concentrations in rural Kolar. *Journal of Family Medicine and Primary Care*, 7(6), 1222–1228.
- Shuval, H. I., & Gruener, N. (2013). *Infant methemoglobinemia and other health effects of nitrates in drinking water*. 183–193.
- Singh, A. L. (2013). Nitrate and phosphate contamination in water and possible remedial measures. *Book: Environmental Problems and Plant Edition: Ist Chapter: Chapter Publisher: Springer Verlag GmbH Heidelberg, Germany Editors: Dwivedi, N*, 44–56.
- Singh, A. S., & Masuku, M. B. (2014). Sampling techniques & determination of sample size in applied statistics research: An overview. *International Journal of Economics, Commerce and Management*, 2(11), 1–22.
- Singh, P., Tiwari, A. K., & Singh, P. K. (2014). Hydro chemical characteristic and quality assessment of groundwater of Ranchi township area, Jharkhand, India. *Current World Environment*, 9(3), 804.
- Sireesha, S., Upadhyay, U., & Sreedhar, I. (2022). Comparative studies of heavy metal removal from aqueous solution using novel biomass and biochar-based adsorbents: Characterization, process optimization, and regeneration. *Biomass Conversion and Biorefinery*, 1–13.
- Skelton, T. (2013). Children, young people, UNICEF and participation. In *Global childhoods* (pp. 165–181). Routledge.
- Smith, B. C. (2011). *Fundamentals of Fourier transform infrared spectroscopy*. CRC press.

- Soares, M., Silva, G., Lima, L., Oliveira, F., Paiva, S., Paulino, M., Júnior, J. R., & Moron, S. (2025). Lack of basic sanitation influence on the enteropathogen presence in a river of the Brazilian Legal Amazon. *Environmental Monitoring and Assessment*, 197(3), 231.
- Speight, J. G. (2020). Sources of water pollution. *Natural Water Remediation*, 165–198.
- Suliman, M. (2017). *Removal of Heavy Metals from Wastewater Using Multiwalled Carbon Nanotubes*.
- Sun, S., & Wang, A. (2006). Adsorption kinetics of Cu (II) ions using N, O-carboxymethyl-chitosan. *Journal of Hazardous Materials*, 131(1–3), 103–111.
- Tadeu, C. M. O., Pujoni, D. G. F., Amado, A. M., Brighenti, L. S., Barros, C. F. de A., Oporto, L. T., Pelegrine, D. dos R., Pereira, G., Cardozo, F. da S., & Pacheco, S. P. (n.d.). Linking Land Use, Seasonal Variation, and Water Quality Through Dom Optical Properties in the Doce River Basin. *Seasonal Variation, and Water Quality Through Dom Optical Properties in the Doce River Basin*.
- Tan, Z., Yao, H., Melack, J., Grossart, H., Jansen, J., Balathandayuthabani, S., Sargsyan, K., & Leung, L. R. (2024). A lake biogeochemistry model for global methane emissions: Model development, site-level validation, and global applicability. *Journal of Advances in Modeling Earth Systems*, 16(10), e2024MS004275.
- Taseidifar, M., Makavipour, F., Pashley, R. M., & Rahman, A. M. (2017). Removal of heavy metal ions from water using ion flotation. *Environmental Technology & Innovation*, 8, 182–190.
- Tecklie, A. T. (2024). Species diversity, some biological aspects of fishes and water quality of Terie River, Beshilo Basin, Ethiopia. *Fisheries and Aquatic Sciences*, 27(6), 356–365.
- Thakur, L. S., & Parmar, M. (2013). Adsorption of heavy metal (Cu²⁺, Ni²⁺ and Zn²⁺) from synthetic waste water by tea waste adsorbent. *International Journal of Chemical and Physical Sciences*, 2(6), 6–19.
- Thapak, H. K., Sharma, J., Boudh, B., Banger, N., Dwivedia, P., & Thapak, H. (2015). Adsorption of copper ions in aqueous media using tea waste and sawdust as an adsorbent. *IJIRST Int J Innov Res Sci Technol*, 2(3), 52–57.
- Thriodore, B. (2004). Interpreting drinking water quality. *Cook College, Rutgers University, New Brunswick*.
- Town, K. K., & Ethiopia, W. (2025). *Assessment of Some Selected Physicochemical and Bacteriological Quality of Water Supply in*.

- Tripathi, M., Agarwal, A., & Mubarak, N. (2023). Heavy metal removal from the wastewater using the tea waste derived bio char synthesized through microwave pyrolysis. *Materials Today: Proceedings*.
- Tyagi, S., Rawtani, D., Khatri, N., & Tharmavaram, M. (2018). Strategies for nitrate removal from aqueous environment using nanotechnology: A review. *Journal of Water Process Engineering*, 21, 84–95.
- Tzou, Y.-M., Wang, S.-L., Hsu, L.-C., Chang, R.-R., & Lin, C. (2007). Deintercalation of Li/Al LDH and its application to recover adsorbed chromate from used adsorbent. *Applied Clay Science*, 37(1–2), 107–114.
- Vakili, M., Deng, S., Cagnetta, G., Wang, W., Meng, P., Liu, D., & Yu, G. (2019). Regeneration of chitosan-based adsorbents used in heavy metal adsorption: A review. *Separation and Purification Technology*, 224, 373–387.
- Vakili, M., Rafatullah, M., Yuan, J., Zwain, H. M., Mojiri, A., Gholami, Z., Gholami, F., Wang, W., Giwa, A. S., & Yu, Y. (2021). Nickel ion removal from aqueous solutions through the adsorption process: A review. *Reviews in Chemical Engineering*, 37(6), 755–778.
- VELEZ, G. (2009). Inductively coupled plasma: The future of heavy metals testing. *Life Science. Technical Bulletin*, 7, 1–2.
- Vivian, O. C., Onuorah, S. C., Agubuokwu, C. V., & Obidinma, N. A. (2024). impacts of seasons on the bacteriological quality of Omambala river at Otuocha in Anambra state, *Nigeria*.
- Vuković, G. D., Marinković, A. D., Škapin, S. D., Ristić, M. Đ., Aleksić, R., Perić-Grujić, A. A., & Uskoković, P. S. (2011). Removal of lead from water by amino modified multi-walled carbon nanotubes. *Chemical Engineering Journal*, 173(3), 855–865.
- Wan, C., & Li, J. (2015). Facile synthesis of well-dispersed superparamagnetic γ -Fe₂O₃ nanoparticles encapsulated in three-dimensional architectures of cellulose aerogels and their applications for Cr (VI) removal from contaminated water. *ACS Sustainable Chemistry & Engineering*, 3(9), 2142–2152.
- Wan, S., Ma, Z., Xue, Y., Ma, M., Xu, S., Qian, L., & Zhang, Q. (2014). Sorption of lead (II), cadmium (II), and copper (II) ions from aqueous solutions using tea waste. *Industrial & Engineering Chemistry Research*, 53(9), 3629–3635.
- Wang, Z., Li, T., Liu, D., Fu, Q., Hou, R., Li, Q., Cui, S., & Li, M. (2021). Research on the adsorption mechanism of Cu and Zn by biochar under freeze-thaw conditions. *Science of The Total Environment*, 774, 145194.
- World Health Organization. (2002). *Guidelines for drinking-water quality*. World Health Organization.

- Wu, H., Wen, Q., Hu, L., & Gong, M. (2018). Effect of adsorbate concentration to adsorbent dosage ratio on the sorption of heavy metals on soils. *Journal of Environmental Engineering*, *144*(2), 04017094.
- Xaplanteris, C., Filippaki, E., Christodoulakis, J., Kazantzaki, M., Tsakalos, E., & Xaplanteris, L. (2015). Cold atmospheric plasma activity on microorganisms. A study on the influence of the treatment time and surface. *Journal of Plasma Physics*, *81*(4), 905810401.
- Xia, Y., Liu, H., Guo, Y., Liu, Z., & Jiao, W. (2019). Immobilization of heavy metals in contaminated soils by modified hydrochar: Efficiency, risk assessment and potential mechanisms. *Science of the Total Environment*, *685*, 1201–1208.
- Yang, D. C., Blair, K. M., & Salama, N. R. (2016). Staying in shape: The impact of cell shape on bacterial survival in diverse environments. *Microbiology and Molecular Biology Reviews*, *80*(1), 187–203.
- Yang, G.-X., & Jiang, H. (2014). Amino modification of biochar for enhanced adsorption of copper ions from synthetic wastewater. *Water Research*, *48*, 396–405.
- Yang, X., Wan, Y., Zheng, Y., He, F., Yu, Z., Huang, J., Wang, H., Ok, Y. S., Jiang, Y., & Gao, B. (2019). Surface functional groups of carbon-based adsorbents and their roles in the removal of heavy metals from aqueous solutions: A critical review. *Chemical Engineering Journal*, *366*, 608–621.
- Yashoda, T., Reddy, T. B., & Ramana, C. V. (2014). Pre-and post-monsoon variation in physico-chemical characteristics in groundwater quality of Mindi industrial area, Visakhapatnam, India. *International Journal of Environmental Sciences*, *4*(5), 746–753.
- Ye, Q., Li, Q., & Li, X. (2022). Removal of heavy metals from wastewater using biochars: Adsorption and mechanisms. *Environmental Pollutants and Bioavailability*, *34*(1), 385–394.
- Yilma, M., Kiflie, Z., Windsperger, A., & Gessese, N. (2019). Assessment and interpretation of river water quality in Little Akaki River using multivariate statistical techniques. *International Journal of Environmental Science and Technology*, *16*, 3707–3720.
- Younas, F., Mustafa, A., Farooqi, Z. U. R., Wang, X., Younas, S., Mohy-Ud-Din, W., Ashir Hameed, M., Mohsin Abrar, M., Maitlo, A. A., & Noreen, S. (2021). Current and emerging adsorbent technologies for wastewater treatment: Trends, limitations, and environmental implications. *Water*, *13*(2), 215.
- Zhang, M., Liu, G., Liu, R., Xu, J., Si, W., & Wei, Y. (2024). High-efficient co-removal of copper and zinc by modified biochar derived from tea stalk: Characteristics, adsorption behaviors, and mechanisms. *Journal of Water Process Engineering*, *57*, 104533.

- Zhang, S., Zhu, X., Zhou, S., Shang, H., Luo, J., & Tsang, D. C. (2019). Hydrothermal carbonization for hydrochar production and its application. In *Biochar from biomass and waste* (pp. 275–294). Elsevier.
- Zhao, H., & Li, Y. (2021). Removal of heavy metal ion by floatable hydrogel and reusability of its waste material in photocatalytic degradation of organic dyes. *Journal of Environmental Chemical Engineering*, 9(4), 105316.
- Zhao, Y.-L., & Stoddart, J. F. (2009). Noncovalent functionalization of single-walled carbon nanotubes. *Accounts of Chemical Research*, 42(8), 1161–1171.
- Zhou, R., Zhang, M., & Shao, S. (2022). Optimization of target biochar for the adsorption of target heavy metal ion. *Scientific Reports*, 12(1), 13662.
- Zhuang, X., Zhan, H., Song, Y., Yin, X., & Wu, C. (2019). Structure-reactivity relationships of biowaste-derived hydrochar on subsequent pyrolysis and gasification performance. *Energy Conversion and Management*, 199, 112014.

APPENDICES

Appendix 1: Pseudo First and Second Order Kinetic Data

Time (min)	Initial Conc. (mg/L)	Ce (mg/L)	qe (mg/g)	qt (mg/g)	qe-qt (mg/g)	ln(qe-qt)	t/qt (min·g/mg)
0	4	4	3.37	0	3.37	1.2149	N/A
10	4	3.2724	3.2724	0.1819	3.0905	1.1283	54.98
20	4	2.967	2.967	0.2583	2.7088	0.9965	77.44
30	4	2.8783	2.8783	0.2804	2.5979	0.9547	106.98
40	4	2.4698	2.4698	0.3826	2.0873	0.7358	104.56
50	4	2.5889	2.5889	0.3528	2.2361	0.8047	141.73

Appendix 2: Langmuir and Freundlich Isotherm Data

Initial Conc. (ppm)	Ce (mg/L)	qe (mg/g)	log Ce	log qe	Ce/qe (g/L)
4	0.8723	0.7819	-0.0593	-0.1068	1.116
6	2.2757	0.9311	0.3571	-0.031	2.444
8	5.5283	0.6179	0.7426	-0.2091	8.947
10	5.3581	1.1605	0.729	0.0646	4.617

Appendix 3: National Commission for Science, Technology & Innovation (NACOSTI) Research Permit




RESEARCH LICENSE

Ref No: 459199

Date of Issue: 22/December/2023



This is to Certify that Miss. GLORY GATWERI GITONGA of Chuka University, has been licensed to conduct research as per the provision of the Science, Technology and Innovation Act, 2013 (Rev.2014) in Meru on the topic: DETERMINATION OF WATER QUALITY STATUS AND THEIR REMEDIATION USING MULTIWALLED CARBON NANOTUBE/HYDROCHAR COMPOSITE IN RIVER KATHITA, MERU, KENYA for the period ending : 22/December/2024.

License No: NACOSTI/P/23/32077

Applicant Identification Number: 459199



Director General

NATIONAL COMMISSION FOR SCIENCE, TECHNOLOGY & INNOVATION

Verification QR Code



NOTE: This is a computer generated License. To verify the authenticity of this document, Scan the QR Code using QR scanner application.

See overleaf for conditions