University of Rwanda

College of Science and Technology

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Assessment of metalloids and heavy metals uptake and their accumulation in soil, wastewater and various plant species from polluted areas by mining activities" Rwinkwavu, Kayonza district, Rwanda

A dissertation submitted to the Department of Chemistry, School of Science, College of Science and technology, University of Rwanda, in partial fulfillment of the requirements for the Degree of Masters in Environmental Chemistry.

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Kigali, June 2025

DECLARATION

I declare that the work titled “Assessment of Heavy Metals Uptake and their Accumulation in Soil, Wastewater, and Various Plant Species from Polluted Areas by Mining Activities in Rwinkwavu, Kayonza District, Rwanda” is my own. I have accurately cited all sources used or mentioned through full citations.

..………………… DATE:…./…./2025

SIGNATURE

Mr HAGENIMANA Emmanuel

MAIN SUPERVISOR CERTIFICATION

I, Dr. ***Gratien HABARUREMA,*** the main supervisor of this master's dissertation entitled "**Assessment of metalloids and heavy metals uptake and their accumulation in soil, wastewater and various plant species from polluted areas by mining activities" Rwinkwavu, Kayonza district, Rwanda"** confirm that it was conducted by Mr. Emmanuel HAGENIMANA under my guidance and supervision. I checked its originality and authorized its submission for examination

Done at Nyarugenge on …………………….

Names of the Main Supervisor and Signature

Dr. Gratien HABARUREMA……………………………………

DEDICATION

To my parents

to my wife

to my children

to my brother and sisters

to my friends

I am thankful to the Lord God for all His blessings, kindness, and mercy.

ACKNOWLEDGEMENTS

I would like to extend my heartfelt gratitude to my supervisors, Dr. Gratien HABARUREMA and Dr. Jean Nepo HAKIZIMANA, for their guidance and meticulous review of the manuscript. Their patience has been invaluable. I also wish to thank the lecturers in the Master's program in Environmental Chemistry at the Department of Chemistry, School of Science, College of Science and Technology, University of Rwanda, for their support throughout my studies.

I also appreciate the support and direction from the WMP LTD mine processing community during sample collections. My thanks extend to the University of Rwanda laboratory technicians, Mr. Emmanuel NKURUNZIZA, Mr. BIRORI MUDAKIKWA Mardochée, and Mr.Vedaste NYANDWI, for their help with sample analysis.

I would like to express my gratitude to the International Science Program (ISP) at Uppsala University, Sweden, for their ongoing support of the Chemistry Laboratory at the University of Rwanda, where I conducted my research. I am also sincerely thankful to my family, friends, and relatives for their love and encouragement throughout this challenging journey. This includes my parents, brothers, sister, and daughters, especially ASHIMWE Louange Eunice and IRAKOZE Gloria Audrey, as well as my wife, ISINGIZWE Bernadette.

The contributions and advice from these individuals have greatly enhanced this project, though I remain responsible for any errors in style, arrangement, facts, or interpretation.

ABSTRACT

Metalloids and heavy metals are considered major contributors to environmental pollution. Mining activities cause metal pollution and soil degradation, impacting nearby organisms through heavy metal absorption by plants. These metals increase disease risk and can be ingested by aquatic life for further spreading contamination. The research aimed to evaluate the uptake and accumulation of metalloids and heavy metals in soil, wastewater, and different plant species in a mining-affected region of Rwinkwavu, Kayonza district, Rwanda. Samples were collected from various locations, including soils, tailings, and wastewater from a nearby river, a processing plant, and a farmer's storage field. Cassava and sweet potato plants, along with their roots, stems, and leaves, were included. Papaya peels were collected for their potential to remove metalloids from the wastewater. Samples were analyzed using standardized laboratory methods, including Flame Atomic Absorption for heavy metals and the Hydride method for metalloids. Bioconcentration and removal efficiency were calculated, and Rstudio software was used for multivariate analysis to identify correlations among heavy metals and metalloids such as arsenic (As), lead (Pb), chromium (Cr), cadmium (Cd), nickel (Ni), copper (Cu), manganese (Mn), and zinc (Zn) across various environmental matrices. Robust ANOVA with post-hoc tests compared contaminant levels across sampling sites, while correlation analysis explored relationships between different heavy metal concentrations. Soil pH at the mining site ranges from moderately acidic (4.47) to neutral (7.09), with tailings showing low cation exchange capacity (CEC1.3-3.3 cmol(+)/kg). Arsenic contamination is notably high, with concentrations from 5.64 mg/kg to 546 mg/kg, and significant positive correlations between Cu, Pb, and As are expected, especially at tailing sites. In wastewater, arsenic levels peak at 1.675 mg/L in the farmer's storage field. Sweet potatoes exhibit high chromium accumulation in tubers (318.4 mg/kg), while cassava shows moderate levels in roots (45.56 mg/kg) and substantial arsenic contamination (80.98 mg/kg). Arsenic in sweet potatoes is mainly found in stems and leaves, and both crops preferentially accumulate manganese in leaves, with cassava having higher concentrations (318.4 mg/kg) than sweet potatoes (223.4 mg/kg). Papaya peel ash demonstrates an arsenic removal efficiency of 80.08%.The study found strong arsenic pollution in the soil and wastewater at the Rwinkwavu mining site, with chromium identified as a hyperaccumulator in farmer's fields. It recommends using papaya peels for metalloid removal and emphasizes on the importance of sustainable environmental management and strategies for managing contamination in the Rwinkwavu mining area.

Key words: Metalloids, heavy metals, bioconcentration, efficiency removal, mining, Rwanda

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LIST OF ABBREVIATION

DNA: Deoxyribonucleic Acid

FAO: Food and Agriculture Organization of the United Nations

GDP: Gross Domestic Product

GPS: Global Positioning System

H_2O_2: Hydrogen Peroxide

H_2SO_4: Sulfuric Acid

$K_2Cr_2O_7$: Potassium Dichromate

LOD: Below the Limit of Detection

NA: Not Applicable

NaCl: Sodium Chloride

NaOH: Sodium Hydroxide

pH: Potential of Hydrogen

RAB: Rwanda Agriculture and Animal Resources Development Board

TDS: Total Dissolved Solids

WHO: World Health Organization

WMP: Wolfram Mining and Processing

1. INTRODUCTION

1.0. Background introduction

Natural resource exploitation has played a variety of roles in strengthening the economy of both emerging and industrialized countries [1]. Metalloids and heavy metals are used in a variety of industries, leading to an increase in market demand and global production[2]. The extensive mining activities that have developed over the years have occurred without pollution control measures, largely due to the absence of environmental regulations [3]. Small-scale and artisanal mining (ASM) is widespread in many African nations, frequently operating informally and presenting challenges related to environmental and social impacts, as well as legal and regulatory frameworks [4]. Mining operations in Africa are associated with various environmental and social issues, such as water pollution, land degradation, human rights abuses, and the displacement of local communities [5]. Mining operations depend significantly on water which is essential for the functioning of machinery and for maintaining health and safety standards and can exert pressure on nearby water sources [6]. In the concept of "planetary boundaries," heavy metals, whether sourced naturally or produced by human activity, can represent a significant environmental threat, and crossing these thresholds might result in dramatic environmental change [7]. Mining is just one of the methods through which metals are released into the environment [8]. Soil can get contaminated with heavy metals and metalloids from emissions in rapidly growing industrial zones, mine tailings, high-metal waste disposal, and irrigation with wastewater [9]. Mining operations often release heavy metals, chemicals, and other pollutants into surrounding water bodies, which can pollute drinking water sources and negatively impact aquatic ecosystems[10]. The indisposed of mining waste like overburdens, tailings and other hazardous materials can contaminate the surrounding environment [11]. This review will focus on the heavy metals and metalloids such ascopper (Cu), nickel (Ni), cadmium (Cd), chromium (Cr), lead (Pb), manganese (Mn), and zinc (Zn), arsenic (As).

1.1. Problem statement

Heavy metals are regarded as a significant source of environmental pollution because of their substantial effect on ecological quality[12]. Mercury, cadmium, arsenic, chromium, thallium, and lead are examples of heavy metals that have high density and can be harmful even at low concentrations[13]. When heavy metal concentrations in soil are high, the problem becomes substantial[2]. It has been noted that metal pollution and soil degradation from mining can have harmful effects on nearby populations [14]. Heavy metals and metalloids are taken up by vegetables and food products from contaminated soils, deposits on crop portions exposed to contaminated air [15]. Contamination of agriculture and crops by heavy metals and metalloids can have a significant influence on food safety and human health [16]. Vegetation in areas contaminated with heavy metals may display modified metabolic functions, as well as physiological and biochemical processes, leading to diminished growth, decreased biomass yield, and the accumulation of metals[17]. Concerningly, water from the study area's main stream is directly used for agriculture and household supplies by rural populations located near the mine [18]. Heavy metals and metalloids can affect the health of both humans and animals in various ways, including causing mutations, cancer, developmental issues, immune suppression, poor overall health, and decreased reproductive capabilities [19]. People who are exposed to environments that contain Cd have a higher risk of developing diseases such as renal dysfunction, a higher risk of breaking bones, and prolonged exposure to lead during pregnancy can result in disorders related to fetal neurodevelopment[20]. Excessive copper in soils presents health risks for plants, humans, and animals. Long-term exposure to elevated levels of copper and other heavy metals can result in a range of health problems, including skin lesions and cardiovascular diseases [21]. High levels of arsenic exposure can cause a variety of health issues, including skin lesions, neurological disorders, cardiovascular diseases, and cancer [22]. When heavy metals and metalloids potentially enter aquatic environments, they are redistributed throughout the water column, deposited or collected in sediments, and eaten by biota [23]. In this regard, the research will focus on determining the levels of heavy metals and metalloids deposited in soil, wastewater, and plant species in a polluted mining area.

1.2. Research Hypothesis

- Soil near mining areas can become contaminated as a result of the accumulation of heavy metals and metalloids.
- Wastewater produced by mining activities contains a range of metalloids and heavy metals.
- Contamination of plant species is associated with soil near mining areas.
- Papaya peel powder may remove metalloids and heavy metals from wastewater

1.3. General objective

To evaluate the uptake and accumulation of metalloids and heavy metals in soil, wastewater, and different plant species from areas affected by mining activities.

1.3.1. Specific objectives

- Assess the concentrations of metalloids and heavy metals in soil, plants, and wastewater from contaminated mining sites.
- Assess bioaccumulation in various plant tissues (roots, stems, and leaves) of specific plant species.
- Evaluate the effectiveness of papaya peel powder in removing specific heavy metals As, Pb, Cu, Ni) from wastewater

2. LITERATURE REVIEW

2.1. Mining activities in Rwanda

Mining in Rwanda have a long history, dating back to the pre-colonial era when local communities engaged in small-scale mining. During the colonial period, the mining sector was further developed, with the involvement of foreign companies and the establishment of larger-scale operations [24].Rwanda is a major producer of tin, tungsten, and tantalum (the "3Ts") minerals, which are used in various electronic and industrial applications [25]. The mining sector contributes around 3-4% of Rwanda's GDP and is a significant source of export earnings.Tin, tungsten, and tantalite (the mineral source of tantalum) have been mined in Rwanda since the colonial era, with production ramping up significantly in the 2000s as global demand for these "conflict minerals" increased. In 2010, the Rwandan government introduced mining regulations and a licensing system to formalize and improve oversight of the sector, including measures to ensure traceability of the 3T minerals. Small-scale and artisanal mining are crucial in Rwanda's mining activities, with estimates suggesting around 35,000 artisanal miners are active in the country. The government has sought to regulate and support this informal mining activity. Rwanda has also explored the potential for commercial-scale mining of gold, rare earth elements, and other mineral resources in recent years, though development has been limited so far.

2.2. Environmental degradation by mining

Mining operations are among the most destructive activities to the environment globally[26]. The extraction and processing of minerals often lead to different forms of environmental damage, posing challenges for sustainable development. Mining operations, including excavation, land clearing, and waste management, can cause the destruction of natural landscapes, loss of biodiversity, and changes in land use patterns[5]. Mining activities can contaminate surface and groundwater by discharging heavy metals, acids, and other harmful substances, endangering aquatic ecosystems and human water sources[27]. Mining activities, including blasting, crushing, and transportation, can produce dust, particulate matter, and other air pollutants, negatively impacting air quality and human health [28]. Mining can disrupt and fragment natural habitats, leading to the displacement or decline in plant and animal life, along with the disruption of ecosystem functions and services[29]. The generation of significant waste, including overburden, tailings, and hazardous materials, presents significant challenges for disposal and long-term management, potentially resulting in environmental contamination [5].

2.3. Environmental behavior of Arsenic (As)

2.3.1. Arsenic in soil

Arsenic (As) is a naturally occurring metalloid often present in elevated levels in soils near mining sites. It can exist in various oxidation states (As (III) and As (V)) in soils, influencing its mobility and bioavailability[30]. Soil pH significantly influences arsenic speciation and adsorption. Arsenic is more mobile in acidic soils and tends to be less mobile in neutral to alkaline soils [31]. Arsenic can be adsorbed onto various soil components, such as iron (hydr) oxides, aluminum (hydr) oxides, and clay minerals, which can reduce its mobility. Changes in soil redox conditions, pH levels and the presence of competing ions can facilitate the desorption of arsenic, increasing its mobility in the soil [32]. Microorganisms can significantly influence arsenic transformation in soils through processes such as oxidation, reduction, methylation, and demethylation[33]. Plant species, soil characteristics, and environmental conditions all play a role in the success of phytoremediation of arsenic-contaminated soils. These microbial processes can affect the speciation and Arsenic mobility in soil. Some plants can accumulate and tolerate high levels of arsenic in their tissues, making them ideal for phytoremediation.[34].

2.3.2. Arsenic in water

Inorganic arsenic is the predominant form found in natural waters, existing primarily as arsenate (As(V)) and arsenite (As(III))[31]. The speciation of arsenic is significantly impacted by the redox conditions and pH levels of the water [35]. Arsenic can attach to various mineral surfaces, such as iron and aluminum oxides, as well as clay minerals, thereby decreasing its concentration in water. However, changes in pH, redox conditions, and the presence of competing ions can lead to the release of arsenic, increasing its mobility in aquatic environments[36]. Arsenic can precipitate as various mineral phases, such as arsenic sulfides (e.g., orpiment, realgar) and iron-arsenic oxides, depending on the geochemical conditions [31]. Arsenic can co-precipitate with minerals like iron hydroxides, helping to lower its levels in the water column[37]. Microorganisms significantly influence arsenic transformation in aquatic environments through processes such as oxidation, reduction, methylation, and demethylation[33]. Aquatic organisms can accumulate arsenic through the food chain, leading to bioaccumulation in higher trophic levels[38].

2.3.3. Arsenic in plant

Plants can take up arsenic from the soil through their roots, mainly as inorganic arsenic species like arsenate and arsenite. Factors like soil arsenic levels determine the amount of arsenic that plants absorb and deposit, soil characteristics (including pH, redox conditions, and organic matter), and the specific plant species involved [39]. Once absorbed, arsenic can be transported from the roots to the shoots and other tissues via the vascular system. Its distribution inside the plant might vary, with higher quantities usually found in the roots, then in the leaves, stems, and finally in the grains or fruits. Some plant species have the ability to sequester arsenic in specific tissues, such as cell walls or vacuoles, as a protective strategy[40]. The speciation of arsenic in plant tissues is important because different forms exhibit varying levels of toxicity and bioavailability. Inorganic arsenic species, Arsenate and arsenite are usually more poisonous than organic versions like dimethylarsinic acid (DMA) and monomethylarsonic acid (MMA). Some plants can transform inorganic arsenic into less toxic organic forms through methylation and other metabolic processes [41]. High concentrations of arsenic in plant tissues can negatively affect plant growth, photosynthesis, and other physiological processes. Plants have evolved multiple protection mechanisms, including the production of antioxidants and phytochelatins, to counteract the toxic effects of arsenic. Some species, referred to as hyperaccumulators, can tolerate and accumulate extremely high levels of arsenic in their tissues without suffering significant toxicity [42].

2.4. Environmental behavior of Cadmium (Cd)

2.4.1. Cadmium in soil

Soils in areas with historical or ongoing mining activities often exhibit elevated concentrations of cadmium. Cadmium concentrations in soils impacted by mining activities can vary significantly, typically ranging from a few milligrams per kilogram (mg/kg) to several hundred mg/kg, influenced by factors such as the specific mining methods used, the composition of the ore, and historical waste disposal practices[43]. Cadmium (Cd) is a toxic heavy metal that can accumulate in soils, posing major concerns to both the environment and human health.[44]. Several factors influence cadmium's movement and behavior in soil, including soil pH, the amount of organic matter, clay content, and the presence of other metals[43]. Soil pH plays a vital role in the mobility and bioavailability of cadmium. Typically, lower pH levels (more acidic conditions) lead to increased solubility and availability of cadmium in the soil [45]. Lower pH values promote the release of cadmium from soil particles, thereby enhancing its availability for absorption by plants and increasing the likelihood of leaching into water sources [46].

Organic matter in soil can create stable complexes with cadmium, which helps to decrease its mobility and bioavailability [47]. The presence of organic matter can enhance the cation exchange capacity of soil, improving its ability to absorb cadmium and other heavy metals [48]. The behavior of cadmium in soil can be affected by the presence of other metals, such as copper (Cu) and zinc (Zn). These metals' competitive adsorption may change each one's mobility and bioavailability [49].

2.4.2. Cadmium in wastewater

Mined wastewater, or mine drainage, is a significant factor in heavy metal pollution, including cadmium (Cd), resulting from the extraction and processing of minerals and ores [50]. The behavior of cadmium in mined wastewater is shaped by various factors, including pH, the presence of complexing agents, and the overall composition of the wastewater. Less soluble precipitates may occur as a result of higher pH levels, such as $Cd(OH)_2$, which can be effectively removed through sedimentation or filtration methods [51]. The existence of complexing agents, including ions, sulfate, and organic matter, can also influence the behavior of cadmium in mined wastewater. The overall composition of mined wastewater, including the presence of additional heavy metals and ions can also influence cadmium's behavior. Competitive adsorption and precipitation processes can occur, which can influence the removal efficiency of cadmium from the wastewater [52].

2.4.3. Cadmium in plant species

Different plant species show varying levels of tolerance to and accumulation of cadmium. Some species, referred to as hyperaccumulators, can absorb remarkably high concentrations of cadmium in their tissues while displaying minimal signs of toxicity [53]. The distribution of cadmium within different plant organs is also an important aspect of its behavior. Cadmium tends to accumulate more in roots than in shoots, since the roots serve as the main point of cadmium absorption from the ground [54]. Higher concentrations in the aboveground biomass, however, may result from certain plant species' ability to translocate a sizable amount of the cadmium absorbed by the roots to the shoots[55]. The behavior of cadmium in various plant species can be greatly influenced by ecological conditions, such as the pH of the soil, the amount of organic matter present, and the presence of other heavy metals. Acidic soil conditions can enhance the bioavailability and absorption of cadmium by plants, while the presence of organic matter can reduce cadmium's mobility and availability [54]. Additionally, the presence of other heavy metals, like zinc or copper, can create competitive interactions that influence cadmium uptake and movement within the plant [55]. Understanding how cadmium behaves in plant species is essential for creating strategies to reduce the risks linked to cadmium contamination in the environment. This includes the use of phytoremediation, where certain plant species are employed to remove or stabilize cadmium in contaminated soils or waters [53].

2.5. Environmental behavior of Chromium (Cr)

2.5.1. Chromium in the soil

There are two primary oxidation states of chromium in the environment: hexavalent chromium (Cr(VI)) and trivalent chromium (Cr(III)).[56]. The speciation of chromium is highly depends on the soil's redox conditions and pH levels [57]. Due to its propensity to stick to soil particles, trivalent chromium (Cr(III)) is normally less mobile in soil, including clay minerals and iron oxides [58]. Hexavalent chromium (Cr(VI)) is more mobile in soil and can easily be desorbed, particularly under alkaline conditions [59]. Trivalent chromium (Cr (III)) can precipitate as chromium (III) hydroxide ($Cr(OH)_3$) or co-precipitate with other minerals, such as iron oxides, reducing its mobility in the soil [59]. Hexavalent chromium (Cr(VI)) can also precipitate as calcium chromate ($CaCrO_4$) or barium chromate ($BaCrO_4$) in the presence of suitable cations[57]. Microorganisms and organic matter in the soil can reduce hexavalent chromium (Cr(VI)) which is converted to the less toxic and less mobile trivalent chromium (Cr(III)) [60]. However, in the presence of potent oxidizing agents such as manganese oxides, trivalent chromium (Cr(III)) can be converted to hexavalent chromium (Cr(VI)).[59]. Trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)) can both be absorbed by plants; the latter is more readily absorbed and may lead to higher bioaccumulation [61]. The degree of chromium uptake and bioaccumulation in plants is influenced by several factors, including soil characteristics, plant species, and the form of chromium present.

2.5.2. Chromium in water

Trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)) are the most common oxidation states of chromium in aquatic settings. The relative proportions of chromium species are affected by factors like pH, redox potential, and the presence of complexing agents [62]. Trivalent chromium (Cr(III)) has low solubility and tends to form insoluble hydroxides or precipitate with other ions, reducing its mobility in aquatic systems [59]. Hexavalent chromium (Cr(VI)) is typically more toxic and more readily available to aquatic organisms than trivalent chromium (Cr(III)). The bioaccumulation and toxicity of chromium in aquatic ecosystems are influenced by several factors, including the form of chromium, water chemistry, and the sensitivity of the organisms involved[63].

2.5.3. Chromium in plant species

Trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)) found in the soil can both be absorbed by plants through their roots, while hexavalent chromium is often more easily absorbed[63]. The movement of chromium from the roots to the shoots and leaves varies among plant species, with some plants displaying higher chromium accumulation in aerial biomass [61]. Certain plant species, referred to as hyperaccumulators, can endure and store remarkably high concentrations of chromium in their tissues, typically ranging from 1,000 to 10,000 mg/kg of dry weight[53]. Examples of chromium hyperaccumulator plants include Leersiahexandra, Pterisvittata, and Athyriumyokoscense. Other plants, known as excluders, can limit the uptake and translocation of chromium, thereby reducing its accumulation in aboveground biomass [64]. The capacity of specific plant species to tolerate and accumulate high levels of chromium makes them ideal candidates for phytoremediation of chromium-contaminated soils and water sources [53]. Successful phytoremediation using chromium-tolerant plants has been demonstrated in various mine and industrial sites [61]. Exposure to chromium can lead to a range of physiological and biochemical changes in plants, including stunted growth, chlorosis, oxidative stress, and changes in enzyme activities. However, some plants have evolved mechanisms to counteract these negative effects, such as producing antioxidants, chelating agents, and proteins that bind chromium [64]. Chromium accumulation and tolerance can differ greatly among various plant species and even within the same species. This variation can be attributed to factors such as root system architecture, metal exclusion mechanisms, and differences in chromium speciation and bioavailability in the soil.

2.6. Environmental behavior of Copper (Cu)

2.6.1. Copper in soil

Copper is an element that naturally exists in the Earth's crust and is often found in elevated concentrations in areas related to mining and mineral processing [8]. Mining and smelting activities can lead to the accumulation of copper in surrounding soils, often in the form of copper sulfides, oxides, and other mineral forms [65]. In acidic environments, copper is more soluble and mobile, whereas in neutral to alkaline conditions, it can form less soluble complexes and precipitate. Soil minerals, including clay, iron, and aluminum oxides, can strongly adsorb and retain copper, limiting its mobility in the soil [8]. Plants can readily absorb copper from the soil, and excessive copper levels can lead to phytotoxicity, causing growth inhibition, chlorosis, and other adverse effects. A number of variables, including soil pH, organic matter level, and the presence of both essential and non-essential minerals, affect the bioavailability and absorption of copper by plants [66].

2.6.2. Copper in water

Copper has limited solubility in water, with a maximum concentration of soluble copper ions (Cu^{2+}) being around 1 mg/L at neutral pH [67].The solubility of copper increases as the pH decreases, as more copper ions are released into the water. Copper can exist in two main oxidation states in water: cupric (Cu^{2+}) and cuprous (Cu^{+}) [68]. The cupric ion (Cu^{2+}) is the more stable and common form in natural waters. Copper can precipitate as copper hydroxide, copper carbonate, or copper sulfide, affected by the water's pH level and the presence of other dissolved ions. Its toxicity to aquatic organisms is affected by factors such as water hardness, pH, and the presence of other compounds [69].

2.6.3. Copper in plant

Through their root systems, plants can take copper from the soil. A number of variables, such as the pH, organic matter, soil copper content, and plant species, affect how much copper accumulates in plant tissues [70]. Some plant species are classified as copper hyperaccumulators because they can gather extremely high levels of copper in their aboveground tissues. Copper toxicity can impair photosynthesis, respiration, and other physiological processes in plants. At the cellular level, excess copper can cause oxidative stress, disrupt membrane integrity, and interfere with the function of essential enzymes and proteins [66].

2.7. Environmental behavior of Lead (Pb)

2.7.1. Lead in soil

Mining and mineral extraction processes, including ore extraction, beneficiation, and smelting, can introduce lead into the surrounding environment. Lead-containing ores, tailings, and waste materials can contaminate nearby soils. Past mining practices, which involved the use of lead-based compounds, can also lead to the accumulation of lead present in soils[50]. The transport and bioavailability of lead in mining soils are influenced by factors such as soil pH and the content of organic matter, and the presence of other minerals. In acidic mining soils, lead can be more soluble and accessible, increasing the risk to human health and the environment. Adding certain soil amendments, such as lime or organic matter, can help stabilize lead and lower its bioavailability [71]. High lead levels in mining soils can negatively impact soil ecosystems, leading to reduced microbial activity, stunted plant growth, and the bioaccumulation of lead within the food chain. Human exposure to lead-contaminated mining soils can occur through direct contact, inhalation of dust, or ingestion of contaminated food or water. Lead exposure can pose significant health risks, particularly for children, including neurological, developmental, and other adverse effects [65].

2.7.2. Lead in water

Lead is a common contaminant found in wastewater generated from mining operations as a result of extracting and processing ores and minerals that contain lead [72]. The dynamics of lead in mine wastewater are affected by a range of physical, biological and chemical components. It can exist in different chemical forms (species) in mine wastewater, including Pb^{2+}, $PbOH^{+}$, and Pb-carbonate complexes, based on the pH level, redox conditions, and the availability of other ions [73]. The solubility of lead species in water is a crucial factor in determining its mobility and bioavailability. It can precipitate as insoluble compounds, such as lead hydroxide or lead carbonate, under specific pH and geochemical conditions [52]. The degree of lead adsorption is influenced by variables including pH, ionic strength, the existence of competing ions, and the characteristics of the surfaces that adsorb lead [74]. Microbial processes, such as oxidation, reduction, and methylation, can alter the speciation and mobility of lead in mine wastewater. The guideline for the selected heavy metals in drinking water is set at 0.01 mg/l (Table 1). Certain microorganisms can also accumulate lead or facilitate its precipitation, This may have an impact on how lead behaves and is distributed in aquatic environments[75].

Table 1.Permissible limits for drinking water [76]

Heavy metal/metalloid	**WHO (mg/l)**
Arsenic As)	0.01
Lead (Pb)	0.01
Cadmium (Cd)	0.003
Mercury (Hg)	0.006
Chromium (Cr)	0.05
Nickel	0.07

2.7.3. Lead in plant species

Plants can absorb lead from the soil, water, and air in mined areas and accumulate it in various plant tissues (e.g., roots, stems, leaves). Once absorbed, lead can be transferred from the roots to the aerial sections of the plant parts, such as stems and leaves, through the vascular system [77]. The lead distributed within the plant is influenced by the plant's internal transport mechanisms and the plant's ability to sequester or exclude lead in certain tissues [78]. High levels of lead can cause various phytotoxic effects in plants, including reduced growth, chlorosis (yellowing of leaves), necrosis (cell death), and decreased photosynthetic activity [77]. The severity of lead toxicity based on the plant species, the level of lead concentration, and the length of exposure. Some plant species that can accumulate high levels of lead without significant toxicity symptoms are used in phytoremediation, a method that uses plants to extract, transport, stabilize, or break down pollutants in the environment [79].

2.8. Environmental behavior of Zinc (Zn)

2.8.1. Zinc in soil

Soils in regions where mining occurs typically show increased zinc levels because of the extraction and treatment of ores that contain zinc [80]. The amount of zinc found in soils affected by mining can differ significantly based on the specific mining operations conducted, geological characteristics, and the degree of soil contamination [81]. The chemical speciation of zinc in mined soils, such as its association with organic matter, clay minerals, or metal oxides, can influence its bioavailability and mobility [80]. Zinc speciation and availability in mining-impacted soils can be influenced by factors like cation exchange capacity, redox potential, and soil pH[82]. Plants can take up zinc from the soil via their roots and transport it to their aerial portions [81]. The degree of zinc uptake and accumulation differs among various plant species and is affected by factors like plant physiology, soil characteristics, and the presence of other heavy metals. Elevated zinc levels in mined soils can be toxic to plants, resulting in stunted growth, chlorosis (yellowing of leaves), and decreased biomass production [82]. The severity of zinc toxicity varies according to the plant species, the concentration of zinc in the soil, and the presence of other heavy metals or nutrients [80]. Certain zinc-accumulating plant species are utilized in phytoremediation, a method that employs plants to eliminate, transport, stabilize, or break down environmental contaminants. These plants can help remediate soils and waters contaminated with zinc in mined regions [81].

2.8.2. Zinc in water

Mine wastewater frequently has high concentrations of zinc as a result of the extraction and processing of ores that contain zinc [8]. The concentration of zinc in mine wastewater can vary greatly, influenced by aspects including the kind of mining operation, the mineral composition of the ore, and the characteristics of the wastewater treatment methods employed. The speciation of zinc in mine wastewater, such as its association with dissolved organic matter, inorganic ligands, or the formation of precipitates, can influence its mobility and bioavailability [83]. Alterations in environmental conditions, such as pH, can cause zinc to desorb from surfaces, increasing its mobility and potentially enhancing its bioavailability. Aquatic organisms, such as algae, invertebrates, and fish, can absorb and accumulate zinc from mine wastewater through various exposure routes, including direct uptake from the water and dietary intake [8]. The extent of zinc bioaccumulation in aquatic organisms depends on the zinc concentration, its bioavailability, and the organism's physiology and feeding habits. Zinc is harmful to many aquatic organisms at concentrations ranging between 0.1 and 1.0 mg/L, leading to effects such as stunted growth, reproductive impairment, and increased mortality[84].

2.8.3. Zinc in plant species

The movement of zinc within the plant, from the roots to the shoots, is facilitated by specific zinc transporters and chelating agents [85]. Once absorbed, zinc can be translocated to different plant tissues, with the distribution varying among plant species, growth stages, and environmental conditions. Certain plant species, referred to as hyperaccumulators, can gather notably high concentrations of zinc in their aboveground tissues without exhibiting major symptoms of toxicity[86]. The soil's pH level and the quantity of organic matter present have an impact on the availability and uptake of zinc by plants, variations among plant species, growth stages, and interactions with other metals [87].

2.9. Environmental behavior of Nickel (Ni)

2.9.1. Nickel in soil

Nickel mainly occurs in the +2 oxidation state (Ni^{2+}) in the environment, which is the most stable and bioavailable form for plants and microorganisms [88]. In polluted soils, nickel can be present in various forms, including soluble salts, oxides, and complexed with organic matter, which affects its mobility and bioavailability [89]. The amount of organic matter, pH, and other metals present all have an impact on the bioavailability of nickel in soil. Lower pH levels typically enhance nickel solubility, making it more accessible for uptake by plants and microorganisms [88]. High concentrations of nickel can adversely affect soil microbial communities, leading to reduced microbial diversity and activity. This can interfere with vital soil functions, including nutrient cycling and organic matter decomposition. Nickel toxicity can also affect soil fauna, such as earthworms, which are essential for soil health and structure. High concentrations of nickel may result in reduced earthworm populations and changes in soil dynamics [90]. Various bioremediation techniques, such as phytoremediation, are being explored to mitigate nickel contamination in soils. This involves using plants that can tolerate and accumulate nickel, thereby reducing its concentration in the soil. Enhanced plant-based bioremediation techniques, which may involve the use of soil amendments or microbial inoculants, can improve the effectiveness of phytoremediation strategies [90].

2.9.2. Nickel in plant

Because it is an essential part of several metalloenzymes, nickel is a necessary element for plant growth, including urease, which is essential for nitrogen metabolism. It also plays important roles in the activity of Ni-Fe hydrogenase and superoxide dismutase[91]. Although nickel deficiency is rare, it can lead to symptoms such as reduced urease activity, which may cause necrosis in leaf tips [92].High levels of nickel can be toxic to plants, leading to various physiological and biochemical disruptions. Symptoms of nickel toxicity include inhibited germination, reduced chlorophyll content, and oxidative stress [93]. Excessive buildup of nickel causes oxidative stress by increasing the generation of reactive oxygen species (ROS), which can harm cellular structures and disrupt metabolic processes[92]. Plants have evolved several mechanisms to manage nickel stress, including the activation of antioxidant defense systems. Enzymes including peroxidase (POD), catalase (CAT), and superoxide dismutase (SOD) are part of these systems, which help reduce oxidative damage. Additionally, specific plant-bacterial associations can improve nickel tolerance.For instance, nickel hyperaccumulator plants often form beneficial relationships with specific rhizobacteria that help mitigate nickel toxicity [93].

2.9.3. Nickel in water

Nickel can enter water bodies through mining operations, where it is often found in ores. The extraction and processing of nickel can lead to its release into the environment, especially in regions with inadequate waste management practices. In mining-impacted regions, groundwater and surface water can become contaminated with nickel due to runoff and leaching from tailings and waste rock[94]. Nickel is recognized as toxic even at low concentrations. Extended exposure to nickel can result in significant health issues, including respiratory problems, kidney diseases, and possible carcinogenic effects [95]. The permissible limit for nickel in drinking water is 0.01 mg/L, whereas the industrial discharge limit for wastewater is established at 2 mg/L [96]. The mechanisms by which nickel is removed from wastewater typically involve surface complexation, cation exchange, and electrostatic interactions. The properties of the adsorption process are reflected in the adsorption behavior, which generally agrees with models such as the Freundlich and Langmuir isotherms [97].

2.10. Environmental behavior of Manganese (Mn)

2.10.1. Manganese in soil

Manganese exists in various oxidation states, primarily as Mn^{2+} in acidic conditions and as Mn oxides in neutral to alkaline conditions. The solubility and availability of manganese to plants are significantly affected by soil pH.In acidic soils, manganese is more soluble and easily available for plant uptake, whereas in alkaline soils, it tends to precipitate as insoluble oxides, which decreases its availability [98]. The growth and development of plants depend on manganese. It is essential for respiration, photosynthesis, and the production of certain enzymes.A deficiency in manganese can result in symptoms such as chlorosis, necrosis, and stunted growth in plants[99]. Manganese undergoes biogeochemical cycling in soil, which is influenced by microbial activity. Manganese-oxidizing bacteria can transform soluble Mn^{2+} into insoluble MnO_2, impacting its availability to plants[100]. The cycling of manganese is also associated with the decomposition of organic matter, which can release manganese back into the soil solution, making it accessible for plant uptake[98]. Manganese is essential for plant growth, but both deficiency and toxicity can occur. Deficiency typically manifests in younger leaves as interveinalchlorosis, while toxicity can lead to symptoms such as leaf curling and necrosis [100].

2.10.2. Manganese in plant

Manganese is primarily absorbed by plant roots in its divalent form (Mn^{2+}). The uptake is mediated by specific transport proteins that regulate Mn homeostasis within the plant. This regulation is essential, as both deficiency and excess of Mn can lead to significant physiological issues [101].In many plant species, manganese concentrations usually vary between 20 and 500 (ppm) in dry weight. However, concentrations above 200 mg/kg can be indicative of potential toxicity, particularly if accompanied by symptoms of manganese toxicity in the plant [102]. High levels of manganese can interfere with the uptake and transport of other essential nutrients, influencing magnesium (Mg), iron (Fe) and calcium (Ca). This disruption occurs because excess manganese can compete with these nutrients for uptake sites in plant roots, leading to deficiencies that further impair plant health [103].

2.10.3. Manganese in water

Manganese enters wastewater from mining operations, metal processing, battery manufacturing, and certain chemical industries contribute significant manganese loads to wastewater [104]. Domestic wastewater typically contains manganese concentrations ranging from 0.01-0.5 mg/L, while industrial wastewater can contain concentrations exceeding 10 mg/L [105]. Manganese behavior in wastewater is largely governed by its complex redox chemistry. It primarily exists in four oxidation states: Mn^{2+}, Mn^{3+}, Mn^{4+}, and Mn^{7+}, with Mn^{2+} and Mn^{4+} being the most significant forms in the environment. Under reducing conditions (low dissolved oxygen, negative ORP), manganese exists predominantly as soluble Mn^{2+}. As redox potential and pH increase, manganese oxidizes to form insoluble oxides and hydroxides (primarily MnO_2), which precipitate from solution [106]. The pH-dependent solubility of manganese compounds follows a characteristic pattern, with solubility decreasing as pH increases. Soluble Mn^{2+} predominates at pH < 6, while various oxidized forms (Mn^{3+}, Mn^{4+}) occur at higher pH values, typically forming insoluble oxides and hydroxides [105].

2.11. Effectiveness of papaya peel adsorbents in removing arsenic (As) from wastewater

2.11.1. Introduction

Arsenic poisoning in water is a major environmental and public health concern due to its toxicity and carcinogenic traits.Traditional arsenic removal techniques, including chemical precipitation, ion exchange, and membrane filtration, can be expensive and often produce secondary waste. In contrast, biosorption using agricultural waste materials, such as papaya peels, has emerged as a sustainable and cost-effective alternative. Papaya peels contain abundant functional groups, including carboxyl, hydroxyl, and amine, which enhance the adsorption of arsenic ions. This review examines the potential of papaya peels as a biosorbent for removing arsenic from wastewater.

2.11.2. Functional Groups and Biosorption Mechanism

Papaya peels possess functional groups that facilitate the adsorption of arsenic species (As (III) and As (V)) through processes like ion exchange, complexation, and electrostatic attraction. Additionally, the presence of cellulose, hemicellulose, and lignin in papaya peels increases their adsorption capacity [107].

2.11.3. Effect of Pretreatment

Pretreatment methods, such as chemical modification or thermal activation, have been shown to improve the adsorption efficiency of papaya peels. Acid or alkali treatment increases the availability of binding sites, while carbonization enhances surface area and porosity [108].

2.11.4. Adsorption ability and efficiency

Research has shown that papaya peels possess a significant adsorption capacity for arsenic, with a maximum capacity of 12.5 mg/g for As(III) and 14.2 mg/g for As(V) under optimal conditions (pH 6, 25°C, and a contact time of 120 minutes) [109]. The efficacy of arsenic removal is regulated by pH, initial arsenic concentration, and adsorbent quantity.

2.11.5. Kinetics and Isotherm Analyses

The rate-limiting element is chemisorption, as the adsorption process often follows pseudo-second-order kinetics.The Langmuir isotherm model frequently offers a superior fit compared to the Freundlich model, implying monolayer adsorption on a uniform surface [109].

2.11.6. Comparative Studies

Papaya peels have been compared with other biosorbents, such as banana peels, orange peels, and rice husks, for arsenic removal. In many cases, papaya peels exhibit comparable or superior performance due to their unique chemical composition [107].

2.11.7. Regeneration and Reusability

Papaya peels can be regenerated using mild acids or bases, with minimal loss in adsorption capacity over multiple cycles. This makes them a sustainable option for long-term use in wastewater treatment [108].

3. MATERIALS AND METHODS

3.0. Introduction

This research was carried out in an agricultural area and along a river bank where mining is a major activity. Soil samples, plant samples, water samples were gathered from both the mining site and the surrounding regions affected by the mining operations, as well as along major road streams. Plant samples were collected according to their coverage in the area. Evaluating how mining operations affect the surrounding ecosystem, including the soil, vegetation, and water bodies, seems to be the goal.The sampling approach targets both the mining area itself as well as the downstream/surrounding areas that may be affected by mining operations and mine drainage. The heavy metals and metalloids covered in this review include arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni), manganese (Mn), and zinc (Zn).

3.1. Study area

The Rwinkwavu mining site is located in the Kayonza District within the Eastern Province of Rwanda, latitude: 1° 55' 27" S, longitude: 30° 35' 55" E, it has a month with the least rainfall receives less than 60 mm (2.4 in) of precipitation, making up less than 4% of the total annual precipitation. The concession area is covering a total area of 8,250 hectares and the samples have taken within the area as indicated in figure1. Currently Wolfram Mining and processing ltd (WMP Ltd) is operating the Rwinkwavu mine, which encompasses six sectors within the Kayonza District of Eastern Province: Rwinkwavu, Mwili, Nyamirama, Murama, Kabarondo, and Gahini. The mining activities in the concession are divided into seven zones: Gahengeri, Gahushyi, Nyarunazi, Rutonde, Kibaya, Gihinga, and Migera (see Figure 1), all focused on extracting cassiterite (tin ore). The Rwinkwavu deposits were first discovered in the 1930s by the GARGARATHOS brothers. Mining operations began in 1939 under MOSS, RIDELL, De BORGHRAVE, and GASTRELL, and were later streamlined under DMPG in 1942.In 1945, GEORWANDA (a branch of GEOMINES Co of Zaire) took over the mining operations.

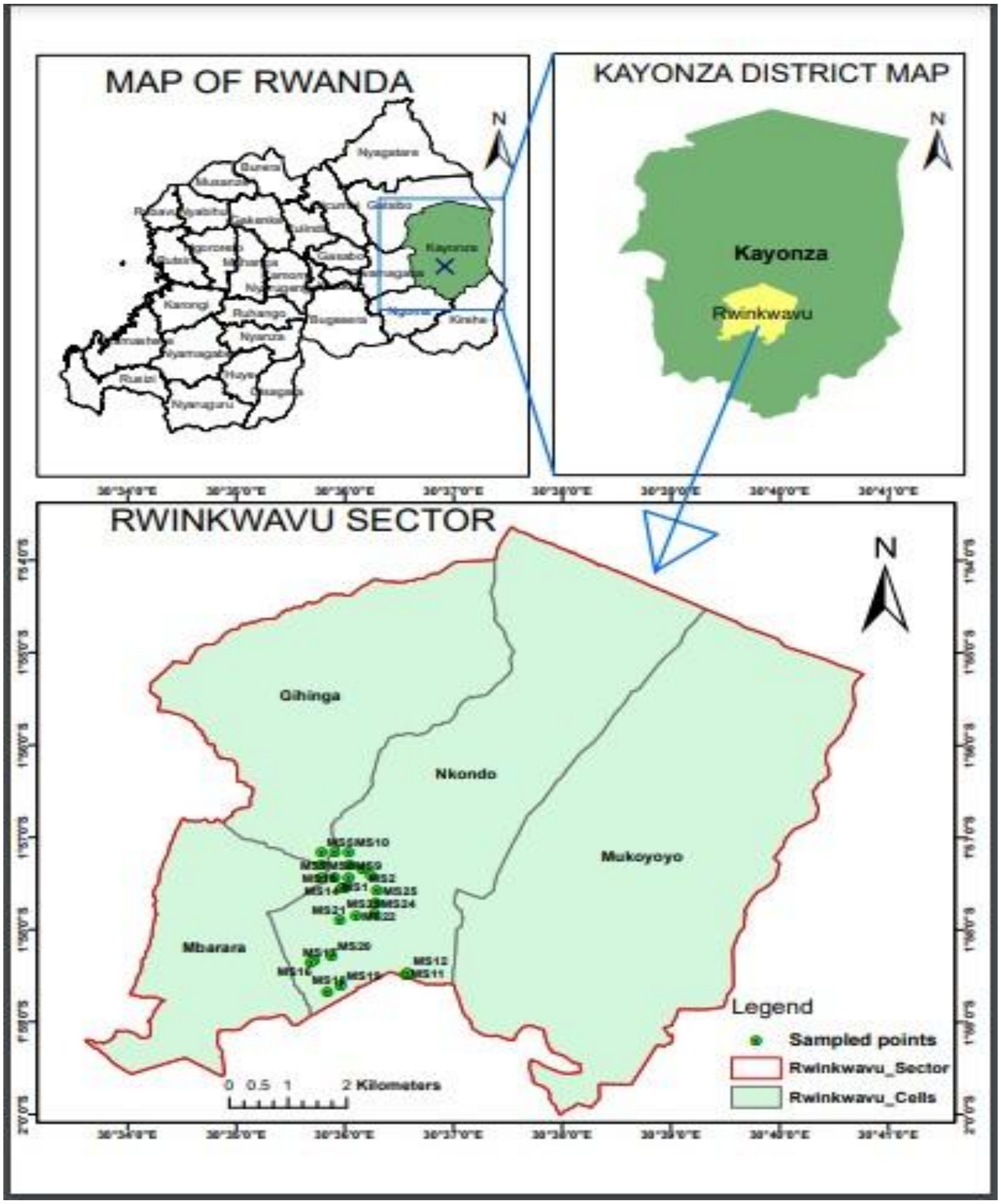

Figure 1. Approach used for sampling plan.

3.2. Data collection

3.2.1. Soil sampling and preparation

Randomly 25 composite soil samples including 5 tailing samples and 20 soil samples were collected in area where mining activities is taking place. The topsoil samples at a depth of 20 cm have been collected using a stainless steel auger. The sub-samples were collected from randomly chosen location with interest and these subsamples were combined or "composited" to create a representative sample for analysis [110]. Each sample was placed in own clean polyethylene bags or container and labeled. A Garmin GPSMAP 64 was utilized to determine the location of each representative soil sample. The samples were taken to the analytical laboratory at RAB Rubona station for the analysis of soil, plant, and wastewater.

The wet soil samples were left to dry in the air at room temperature to eliminate moisture. Once dried, the samples were ground using a mortar and pestle to break down aggregates and ensure homogeneity. The ground soil was then passed through a sieve with a mesh size of 2 mm to remove any coarse particles [111]. The sieved soil samples are then used for further analysis.

3.2.2. Plant tissue sampling and preparation

Randomly 30 plant tissue samples will be collected where soil samples will be taken; including 15 tissue samples for sweet potatoes and 15 tissue samples for Cassava. Each crop separately will have5 leaves, 5 tissues and 5 roots samples. The plant tissue samples will be sampled for bioaccumulation analysis due to part of plant in polluted mine. The samples will be dried in an oven at 60 °C for 48 hours, after which they will be milled for further analysis of metalloids and heavy metal content.

3.2.3. Collection and preparation of wastewater samples

9 representative water samples were taken including 3 wastewater samples from nearby river where mining is taking place, 4 wastewater samples in tailing process and 2 water samples in deposited water then the samples were kept in clean plastic bottle with labels in refrigerator at $4^{o}C$ to preserve its integrity until it will be analyzed in the laboratory.

3.2.4. Papaya peels sampling and preparation

The papaya peels were collected on local market at huye and were transported at analytical laboratory for preparation. All of the samples were properly washed repeatedly with distilled water to remove dirt, debris, and any remaining fruit pulp, and were rinsed multiple times to ensure that the peels were free from contaminants. The peels were dried in an oven at $60^{o}C$ for 48 hours until completely dry. The peels were cooled and ground with a mechanical grinder, then passed through a 0.125 mm mesh to create a fine powder, ensuring consistent adsorption performance. The powdered peels were carbonized by heating them in a muffle furnace at 450°C for 8 hours to produce biochar, which exhibits increased surface area and porosity. The resulting ash was screened using a 0.125 mm mesh. The prepared papaya peels adsorbent was stored in an airtight container to prevent moisture absorption and contamination.

3.3. Methods

3.3.1. Soil chemical and physical properties

Essential chemical and physical parameters for analyzing contaminated mining sites include pH, organic matter content, particle size distribution, electrical conductivity, exchangeable bases, cation exchange capacity, and concentrations of heavy metals [112].

3.3.1.1. Soil pH in water and Electrical conductivity (EC)

Soil pH was measured in a 1:2.5 soil-to-water suspension (w/v) using a glass electrode pH meter [113]. Soil electrical conductivity was measured in a 1:5 soil-to-water suspension (w/v) using a glass electrode EC meter [114].

3.3.1.2. Exchangeable Bases (Ca, Mg, K and Na) and Cation Exchange Capacity (CEC)

Five grams of soil were weighed into a 50 ml extraction tube after being run through a 2 mm sieve. Following the addition of 33 milliliters of a 1M ammonium acetate ($NH_4C_2H_3O_2$) solution at pH 7, the mixture was agitated for fifteen minutes with a reciprocal shaker. The extracted solution was then centrifuged and filtered through Whatman No. 42 filter paper into a 100 ml volumetric flask. This process of adding 33 ml of 1M ammonium acetate, shaking, centrifuging, and filtering was repeated to ensure sufficient extracted solution to fill the volumetric flask. The extractant was subsequently used to analyze calcium (Ca) and magnesium (Mg) using an atomic absorption spectrophotometer, while sodium (Na) and potassium (K) were analyzed using a flame photometer. In 50 ml extraction tube, 50ml of 96% Ethanol was added, shaked, centrifuged and washed to displace the absorbed Ammonium Acetate. The addition of 33ml of a 10% NaCl was added, shaked and centrifuged and filtered in 100 ml volumetric flask. This step was done twice to obtain sufficient extractant and fill the volumetric flask with a 10% NaCl. An aliquot of 50ml was taken and an addition of 10 ml of 40% NaOH was performed, automatically distillate into boric acid and titrate with a 0.01 HCl[115].

3.3.1.3. Particle size distribution

Fifty (50) grams of soil (< 2 mm) were weighed into a conical flask, and then 125 ml of distilled water and 5 ml of a 20% H_2O_2 solution were added. The mixture was oxidized in a water bath at 90°C for 2 hours. Afterward, the sample was removed and allowed to cool. The addition of a 10 ml Calgon was done followed by a transfer of solution into grinder and grinded for 2 min. Following the transfer of the mixed solution into a graduated cylinder, the volume was increased to 1000 ml by adding distilled water. The cylinder was then covered with a tightly fitting rubber bung, and the suspension was mixed by carefully inverting it ten times.

Two to three drops of amyl alcohol were quickly added to the soil suspension to remove any froth. The hydrometer was then gently placed into the column after 20 seconds, and after 40 seconds, the hydrometer reading was noted, and the temperature of the suspension was taken. The cylinder was then resealed with the rubber bung, and the suspension was left undisturbed for two hours. Following this time, the temperature and hydrometer readings were taken[116].

3.3.1.4. Organic Carbon

After weighing a 0.5 g soil sample that had been sieved through a 0.5 mm screen, 2.0 mL of a 10% (0.34 M) $K_2Cr_2O_7$ solution was added and thoroughly mixed. 5.0 mL of H_2SO_4 was then added right away, and the mixture was let to cool for half an hour. The tube was then filled with 20.0 mL of water, stirred, and allowed to stand overnight. A spectrophotometer set to 600 nm was used to measure the absorbance of the samples and calibration standards.[117].

3.3.2. Soil sample digestion and analysis for metalloids and heavy metals determinations

Add 2.5 g of soil to a 50 ml crucible, followed by 10 ml of aqua regia containing a 3:1 ratio of strong hydrochloric acid (HCl) and nitric acid (HNO_3). The mixture was digested on a hot plate at 95 °C for an hour. After digestion, the mixture was allowed to cool to ambient temperature before being diluted with distilled water to make a final volume of 50 ml. The diluted sample was allowed to settle overnight, and then the supernatant was filtered using Whatman No. 42 filter paper to eliminate any solid residues [118]. The filtered sample was analyzed for metalloids and heavy metals using Atomic Absorption Spectroscopy (FAAS).

3.3.3. Plant sample digestion and analysis for metalloids and heavy metals determinations

During the analysis of plant tissue samples, 0.5 g of ground and milled plant material was weighed into a digestion tube alongside a blank sample. The tubes were placed in a fume hood, and 10 mL of concentrated HNO_3 was added immediately. The solution was then placed on a digestion block for 30 to 45 minutes to facilitate oxidation. After allowing to cool, 4 mL of 20% hydrogen peroxide (H_2O_2) was added, and the solution was reheated on the digestion block until it appeared clear and semi-dry. Once cooled again, the suspension was filtered into a 50 mL volumetric flask to remove insoluble material that could clog the nebulizer. The filtered solution was then diluted with distilled water to the indicated line on the flask [118]. This filtrate is ready for the determinations of metalloids and heavy metals using Flame Atomic Absorption Spectroscopy (FAAS) in the chemistry laboratory at the College of Science and Technology, University of Rwanda.

3.3.3. Wastewater sample digestion and analysis

The wastewater samples each one was thoroughly mixed in their container bottles by shaking. Filter a 50 ml aliquot and transfer it into a digestion tube on the block digester. The concentration of metals in the wastewater was assessed by digesting the sample using 3 ml of concentrated nitric acid (HNO_3) and 3 ml of hydrogen peroxide (H_2O_2) at a temperature below 80°C for 1 hour, until a clear solution was achieved [119]. The digested samples were placed into 100 ml volumetric flasks and diluted with distilled water. The blank sample was processed using the same method as the wastewater samples.Metalloids and heavy metals were determined in wastewater using Flame Atomic Absorption Spectroscopy (FAAS) in the chemistry laboratory at the University of Rwanda's College of Science and Technology.

3.3.4. pH, Electrical and TDS analysis in wastewater

The pH meter (pH 3110SET2) was immersed in wastewater and results were recorded. The combination electrode (ST 100C OHAUS CORPORATION, US) was immersed in wastewater and the measurements of electrical conductivity and total dissolved solids (TDS) were recorded.

3.3.5. Assessment of adsorption efficiency of papaya peels using Atomic absorption Spectrophotometer (ContrAA800)

Fourier-transform infrared spectroscopy (FTIR-Bruker Alpha II) was employed to characterize the adsorbents (papaya peel powder and ash) by identifying the functional groups and chemical bonds that affect their adsorption properties and efficiency in removing contaminants from wastewater [120].

Wastewater from the Rwinkwavu mine was prepared with defined concentrations of metalloids and heavy metals. The pH of the wastewater was adjusted to an optimal range (typically 5-6) using HCl or NaOH. Adsorbent doses of 0.5 g/l, 1 g/l, 2 g/l, 2.5 g/l, and 3 g/l, along with a blank, were added. The mixtures were agitated at 150 rpm for 2 hours at ambient temperature (25°C ± 2°C), and the suspensions were poured into volumetric flasks through Whatman No. 42 filter paper for filtration. The filtrate was then analyzed using the hydride method for Atomic Absorption Spectrophotometry (ContrAA 800).

3.4. Data analysis

3.4.1. Data Exploration

To summarize the descriptive statistics of heavy metal concentrations, standard deviation, mean, median, minimum, and maximum values were computed to illustrate the data and generate a histogram.

3.4.2. Bioconcentration factor (BCF)

The bioconcentration factor was determined by dividing the heavy metal concentrations in plant tissue by those in the soil from the corresponding site [121].

$BCF = C_{plant} / C_{soil}$

Where C_{plant} represents the concentration of heavy metals in plant tissue (mg/kg dry weight), while C_{soil} represents the concentration of heavy metals in soil (mg/kg dry weight). The bioconcentration of each part of plant was done using the same formula stated above. See Table 2 for the interpretation range for bioconcentration factor (BCF) calculated.

Table 2. BCF values interpretation guidelines in plant[122]**.**

BCF range	**Interpretations**
< 0.01	No accumulation
0.01-0.1	Low accumulation
0.1-1.0	Moderate accumulation
> 1.0	High accumulation (hyperaccumulation)

3.4.3. Calculation of removal efficiency

"Removal efficiency" describes how effectively a process can eliminate a specific substance or contaminant from a mixture, system, or environment.

It is typically represented as a percentage, calculated with the following formula:

$$\text{Removal efficiency (\%)} = [(Ci - Cf)/Ci] \times 100$$

Where, Ci = Initial concentration, Cf = Final concentration. Higher removal efficiency signifies a more successful process in lowering the concentration of the unwanted substance.

3.4.4. Statistical Analysis

R software was used for comprehensive statistical analysis of environmental contamination data due to its robust capabilities in handling complex environmental datasets. Key descriptive statistical metrics, including the mean, median, standard deviation, as well as the minimum and maximum values of the dataset, have been computed. The correlation coefficient was calculated to examine relationships between variables. To explore group differences, robust ANOVA with post-hoc tests was performed and generated accompanying tables, which provided insights into the significance of the results, including p-values. This detailed analysis provided a thorough understanding of the characteristics and relationships within the data.

3.4.5. Comparison to Standards

The comparison was made between the concentrations of heavy metals and metalloids in soil, plant tissues, and wastewater samples against relevant soil, plant, and water quality guidelines or standards (e.g., WHO and FAO). Identify any soil, plant and water samples that exceed the established thresholds for heavy metal contamination.

4. RESULTS AND DISCUSSIONS

This chapter presents the results of the collected field data, which encompass levels of metalloids and heavy metals in soil, wastewater, and different plant species, including sweet potatoes and cassava. It also covers the physicochemical properties of both soil and wastewater. Furthermore, all data were subjected to statistical analysis.

4.1. Result presentations

4.1.1. Chemical and physical properties of soil surrounding the mining site

The soil pH at the mining site varies from moderately acidic (4.48) to neutral (7.09). Tailing samples have pH values ranging from 5.4 to 6.6. Electrical conductivity (EC) shows significant variation among sampling locations, with peak values reaching 173.5 µS/cm. Organic carbon content is significantly lower in tailing samples compared to other soil samples. The tailing sites also demonstrate very low cation exchange capacity (CEC) values between 1.3 and 3.3 cmol(+)/kg, with a maximum of 22.48 cmol(+)/kg as indicated in Table 3. Calcium is the predominant exchangeable cation across all sites, subsequently including magnesium, potassium, and sodium. As illustrated in Table 4, the locations of the tailings are dominated by sand soil in structure while remained sites are dominated by sandy loam and Sandy Clay Loam.

The correlation matrix analysis revealed significant relationships among various soil chemical and physical parameters (Table5). The analysis identified several strong positive correlations ($r > 0.8$) among key soil parameters. The most notable correlation was observed between organic carbon content and cation exchange capacity ($r = 0.906$), calcium content showed strong correlations with multiple parameters, including cation exchange capacity ($r = 0.927$), organic carbon ($r = 0.838$), and magnesium ($r = 0.889$).

Electrical conductivity demonstrated strong positive correlations with several parameters, most notably with sodium content ($r = 0.856$) and calcium content ($r = 0.787$) while Magnesium content showed moderate to strong correlations with most parameters, including organic carbon ($r = 0.744$), electrical conductivity ($r = 0.73$), and cation exchange capacity ($r = 0.843$). The correlation between electrical conductivity and organic carbon (r = 0.692. Several parameters showed relatively weak correlations like pH exhibited weak correlations with most parameters, with the strongest being with calcium ($r = 0.346$) and magnesium ($r = 0.34$). Potassium showed moderate correlations with organic carbon ($r = 0.583$).

Table 3. Summary statistics

Parameters	Minimum	Maximum	Average	Median
pH water	4.48	7.09	5.8	5.75
EC(μS/Cm)	10.1	173.5	50.01	35.2
Org.C(%)	0.03	3.34	1.13	0.97
CEC(Cmol(+)/Kg)	1.31	22.48	9.78	8.69
Ca(mg/Kg)	94.4	4599.6	1417.52	791.13
Mg(mg/Kg)	19.04	587.69	195.18	182.05
K(mg/Kg)	16.15	370.99	132.26	103.41
Na(mg/Kg)	0.01	262.5	39.59	7.53

Table 4.Chemical and physical properties of soil surrounding the mining site

Location	pH water	EC(μS/Cm)	Org.C(%)	CEC(Cmol(+)/Kg)	Ca(mg/Kg)	Mg(mg/Kg)	K(mg/Kg)	Na(mg/Kg)	Texture
A(waste tailing on site)	5.42lm ± 0.01	89.77e ± 0.78	0.025r ± 0.001	1.42n ± 0.03	94.40v ± 0.02	19.04n ± 0.15	32.31u ± 0.15	0.05i ± 0.01	Silt Loam
B(pure tailing on site)	5.63j ± 0.05	10.60s ± 0.43	0.035r ± 0.001	2.54m ± 0.04	96.00v ± 0.02	28.63mn ± 0.38	16.15w ± 0.04	0.06i ± 0.01	Loamy Sand
C1(Tailing at processing site)	6.60c ± 0.01	16.00qr ± 0.02	0.055r ± 0.001	3.24l ± 0.04	283.67s ± 0.31	52.36lmn ± 0.55	22.53v ± 0.14	7.53h ± 0.06	Sand
C2(waste after processing)	6.50d ± 0.01	15.08r ± 0.03	0.043r ± 0.006	1.31n ± 0.02	152.87u ± 1.63	24.36n ± 0.39	16.17w ± 0.10	0.04i ± 0.01	Sand
D(Tailing on processing site)	6.19f ± 0.01	15.23r ± 0.26	0.055r ± 0.001	2.49m ± 0.01	293.33r ± 3.06	40.29lmn ± 0.24	22.47v ± 0.25	0.06i ± 0.01	Loamy Sand

M11	5.75i ± 0.05	50.87h ± 0.95	2.635c ± 0.029	22.48a ± 0.03	3601.67d ± 2.08	218.73gh ± 0.37	164.84h ± 1.04	52.27f ± 0.32	Loam
M13	5.56jk ± 0.05	69.67f ± 0.15	2.789b ± 0.010	19.09b ± 0.11	3600.47d ± 1.50	530.40b ± 0.60	370.99a ± 1.00	75.33d ± 0.58	Clay Loam
M14	6.21e ± 0.03	91.17d ± 0.25	1.710f ± 0.023	15.51d ± 0.02	2278.73e ± 0.64	411.75c ± 0.34	128.34k ± 1.16	89.67c ± 0.58	Clay
M15	5.77hi ± 0.04	48.20i ± 0.27	1.091k ± 0.004	9.89f ± 0.01	1334.47i ± 5.50	211.84gh ± 0.21	287.37c ± 0.55	7.50h ± 0.10	Sandy Clay Loam
M40	7.09a ± 0.03	136.60c ± 0.36	1.957e ± 0.021	16.50c ± 0.01	4599.60a ± 1.44	407.37c ± 0.52	199.33f ± 1.15	89.67c ± 0.58	Clay Loam
M41	5.85h ± 0.04	22.75o ± 0.14	0.967l ± 0.015	9.42g ± 0.01	732.60m ± 0.53	127.68i ± 0.49	232.42d ± 0.52	0.14i ± 0.01	Sandy Clay Loam
M6	6.01g ± 0.02	55.27g ± 0.15	0.685n ± 0.005	11.48e ± 0.06	1505.07g ± 1.01	296.13e ± 1.03	141.65j ± 0.56	7.43h ± 0.06	Sandy Clay Loam
M7	5.36m ± 0.05	18.63p ± 0.12	0.516p ± 0.006	3.01l ± 0.01	404.00p ± 1.00	90.03jk ± 0.45	41.71t ± 0.36	7.47h ± 0.06	Sandy Loam
M8	5.50kl ± 0.02	173.50a ± 0.44	3.337a ± 0.031	22.29a ± 0.04	3615.73c ± 2.05	360.64d ± 1.49	118.42l ± 1.25	262.50a ± 0.50	Clay Loam
M9	6.32e ±	139.97b ±	2.109d ±	22.22a ± 0.49	4083.20b	587.69a ±	190.44g	254.73b ± 0.46	Clay

	0.03	0.42	0.018		± 1.06	0.36	± 0.51		
R1 Bottom	5.57jk ± 0.01	40.84k ± 0.28	1.144j ± 0.004	8.69h ± 0.01	995.33k ± 0.61	182.05h ± 1.00	366.25b ± 2.81	7.53h ± 0.06	Sandy Clay Loam
R1 Middle	5.37m ± 0.02	35.20l ± 0.20	1.387i ± 0.006	8.51h ± 0.01	791.13l ± 1.21	76.79jkl ± 0.22	100.00n ± 1.00	7.50h ± 0.10	Sandy Loam
R1 Top	5.21n ± 0.02	30.15m ± 0.23	1.652g ± 0.007	9.81f ± 0.01	677.33n ± 1.15	102.65ij ± 0.57	90.31p ± 0.31	7.57h ± 0.12	Sandy Loam
R2 Top	4.48o ± 0.01	10.10s ± 0.21	0.573o ± 0.003	7.73i ± 0.06	191.80t ± 0.72	41.28lmn ± 0.45	51.64s ± 0.12	7.50h ± 0.10	Sandy Loam
R2 middle	5.50kl ± 0.01	18.57p ± 0.31	0.434q ± 0.005	5.74j ± 0.04	384.67q ± 0.42	62.76klm ± 0.14	74.03q ± 0.15	7.53h ± 0.25	Loamy Sand
R3 Under stadium	5.79hi ± 0.01	27.24n ± 0.21	1.394i ± 0.010	11.31e ± 0.06	1575.13f ± 1.21	256.36f ± 0.56	161.76i ± 1.08	15.17g ± 0.15	Sandy Clay Loam
R4	5.13n ± 0.02	18.71p ± 0.02	0.870m ± 0.005	7.43i ± 0.04	663.37o ± 0.57	104.47ij ± 0.50	96.66o ± 0.61	7.51h ± 0.01	Sandy Loam
R5	5.60j ± 0.01	55.50g ± 0.03	1.581h ± 0.006	5.28k ± 0.03	785.93l ± 0.90	186.57gh ± 0.52	216.04e ± 1.00	0.01i ± 0.01	Sandy Loam
R6	6.82b ± 0.02	44.10j ± 0.04	0.687n ± 0.006	7.52i ± 0.03	1208.27j ± 1.10	238.6fg ± 0.45	103.41m ± 0.52	67.57e ± 0.21	Sandy Clay Loam

R7	5.82hi ± 0.03	16.60q ± 0.02	0.508p ± 0.005	9.56fg ± 0.06	1489.20h ± 1.06	221.01fg ± 1.00	61.29r ± 0.10	7.53h ± 0.06	Sandy Clay Loam
P_value	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	

Table 5.Correlation analysis for soil physico-chemical of polluted mine

Parameters	pH water	EC(μS/Cm)	Org.C (%)	CEC(Cmol(+)/Kg)	Ca(mg/Kg)	Mg(mg/Kg)	K(mg/Kg)	Na(mg/Kg)
pH water	1							
EC(μS/Cm)	0.275	1						
Org.C(%)	-0.036	0.692	1					
CEC(Cmol(+)/Kg)	0.104	0.701	0.906	1				
Ca(mg/Kg)	0.346	0.787	0.838	0.927	1			
Mg(mg/Kg)	0.340	0.73	0.744	0.843	0.889	1		
K(mg/Kg)	0.023	0.308	0.583	0.522	0.501	0.597	1	
Na(mg/Kg)	0.231	0.856	0.694	0.762	0.764	0.743	0.193	1

4.1.2. Level of metalloids and heavy metals of soil surrounding the mining

The dataset provides important insights into the distribution of heavy metals and metalloids such as lead, zinc, copper, and chromium, along with nickel, manganese, and arsenic across various locations in a mining-impacted area. The contamination levels vary significantly between mine sites (M-coded), tailings sites (A, B, C1, C2, D), and reference sites (R-coded), reflecting the heterogeneous nature of mining-related pollution. Table 6 presents the concentrations of measured heavy metals and metalloids.

Lead levels range from 6.22 mg/kg (R2 middle) to 36.44 mg/kg (B-pure tailing site). The tailing sites, Zinc concentrations exhibit extreme variability, ranging from below detection limits at some sites (M41, R2 middle) to 127.84 mg/kg at site M6. Particularly B and C2, show significantly elevated Pb levels compared to most reference sites. Copper concentrations vary between 1.79 mg per kilogram (R2 middle) up to 35.14 mg per kilogram (M14).Chromium concentrations vary considerably across sites, ranging from 0.22 mg/kg (B-pure tailing) to 76.84 mg/kg (R5). The cadmium was below the limit of detection on the obtained results.

Nickel levels vary from 0.31 mg per kilogram (R2 middle) to 14.48 mg per kilogram (R7), and the highest concentration is Ni (14.44 mg/kg) at reference site R7compared to other sites. Manganese shows substantial variation across sites, ranging from 15.41 mg/kg (R2 Top) to 272.61 mg/kg (M14). The most striking contamination pattern in the dataset relates to arsenic, with concentrations ranging from 5.64 mg/kg (R1 Top) to an alarming 546 mg/kg (B-pure tailing). See in table7 the heavy metal correlation analysis among different metallic contaminants and basic soil properties. Lead (Pb) demonstrated the strongest correlation with copper (Cu) at $r = 0.88$ and arsenic (As) exhibited a significant positive correlation with copper ($r = 0.72$). Lead exhibited moderate to strong correlations with several other metals, including chromium (Cr) at $r = 0.54$, nickel (Ni) at $r = 0.60$, manganese (Mn) at $r = 0.60$, and arsenic at $r = 0.68$.

Notably, zinc demonstrated a negative correlation with organic carbon content ($r = -0.34$). Most metals showed weak to negligible correlations with pH, with the exception of lead and chromium, both showing moderate positive correlations with pH ($r = 0.36$). The relationship between heavy metals and cation exchange capacity varied considerably among different metals. While lead revealed a moderate indicated a positive correlation with CEC ($r = 0.39$), while zinc exhibited a negative correlation ($r = -0.12$), and most other metals showed weak relationships.

Table 6.Level of metalloids and heavy metals of soil surrounding the mining site

Location	Pb(mg/kg)	Zn(mg/kg)	Cu(mg/kg)	Cr(mg/kg)	Ni(mg/kg)	Mn(mg/kg)	As(mg/kg)
A(waste tailing on site)	11.191s ± 0.003	13.190l ± 0.011	17.44f ± 0.009	5.806t ± 0.006	5.819j ± 0.001	70.71u ± 0.03	339.12b ± 0.19
B(pure tailing on site)	36.437a ± 0.025	15.740k ± 0.070	15.893fg ± 0.015	0.218u ± 0.001	9.362c ± 0.002	124.21n ± 0.02	545.67a ± 0.42
C1(Tailing at processing site)	15.199l ± 0.008	45.204d ± 0.011	24.940b ± 0.020	45.353h ± 0.031	7.822e ± 0.002	151.96k ± 0.03	77.94i ± 0.04
C2(waste after processing)	35.533b ± 0.050	33.553f ± 0.070	23.080bcd ± 0.010	52.447g ± 0.040	8.876d ± 0.004	234.55c ± 0.13	220.22c ± 0.31
D(Tailing on processing site)	18.783d ± 0.141	31.853g ± 0.070	23.413bcd ± 0.031	58.783f ± 0.025	6.694h ± 0.006	188.02e ± 0.10	128.30e ± 0.34
M11	16.065j ± 0.007	4.439r ± 0.013	13.565hij ± 0.006	32.343l ± 0.015	9.634b ± 0.175	206.44d ± 0.37	<LOD
M13	14.970m ± 0.010	13.483l ± 0.100	15.969fg ± 0.004	40.420j ± 0.040	4.291m ± 0.002	179.70g ± 0.13	<LOD
M14	21.407c ± 0.015	57.107c ± 0.015	35.140a ± 0.020	63.620e ± 0.020	8.806d ± 0.002	272.60a ± 0.02	121.13f ± 0.02

M15	15.663k ± 0.006	27.860h ± 0.072	17.306f ± 3.462	65.633c ± 0.061	7.166g ± 0.007	186.87f ± 0.03	<LOD
M40	16.64i ± 0.010	16.708j ± 0.009	14.777gh ± 0.035	30.610m ± 0.026	5.311k ± 0.010	162.57i ± 0.05	51.05m ± 0.07
M41	10.791t ± 0.003	<LOD	5.695n ± 0.006	29.623n ± 0.025	2.969n ± 0.003	54.20v ± 0.02	15.79p ± 0.00
M6	17.296f ± 0.005	127.513a ± 0.466	20.182e ± 0.002	64.810d ± 0.010	5.883j ± 0.003	133.08m ± 0.03	37.68n ± 0.07
M7	17.806e ± 0.014	42.070e ± 0.046	22.420cd ± 0.026	43.863i ± 0.015	7.641f ± 0.003	176.38h ± 0.03	131.81d ± 0.03
M8	16.813h ± 0.020	9.897n ± 0.015	14.700gh ± 0.020	34.687k ± 1.123	6.339i ± 0.019	259.57b ± 0.06	<LOD
M9	14.195n ± 0.005	10.473m ± 0.010	12.144ijk ± 0.011	34.560k ± 0.020	4.964l ± 0.004	110.53p ± 0.10	<LOD
R1 Bottom	10.792t ± 0.012	7.933o ± 0.004	5.994n ± 0.006	16.334r ± 0.006	2.352o ± 0.001	117.96o ± 0.07	<LOD
R1 Middle	9.090v ± 0.002	5.963q ± 0.010	7.487mn ± 0.003	34.397k ± 0.015	1.352r ± 0.001	133.16m ± 0.13	84.12h ± 0.02

R1 Top	8.881w ± 0.003	7.547p ± 0.016	8.826lm ± 0.004	29.633n ± 0.050	1.662q ± 0.003	46.52w ± 0.03	5.64q ± 0.00
R2 Top	10.677u ± 0.006	1.106t ± 0.006	10.544kl ± 0.004	21.560p ± 0.044	1.734q ± 0.001	15.40x ± 0.01	51.65l ± 0.06
R2 middle	6.224x ± 0.005	0.000 ± 0.000	1.786o ± 0.002	6.861s ± 0.003	0.306s ± 0.002	159.14j ± 0.25	19.23o ± 0.01
R3 Under stadium	13.300q ± 0.010	0.446u ± 0.003	11.463jk ± 0.038	28.743o ± 0.047	2.962n ± 0.002	76.65t ± 0.07	<LOD
R4	17.064g ± 0.011	16.548j ± 0.027	23.713bc ± 0.015	29.817n ± 0.015	4.380m ± 0.002	104.61q ± 0.09	100.26g ± 0.34
R5	13.606p ± 0.011	23.123i ± 0.015	21.303de ± 0.015	76.687a ± 0.133	1.883p ± 0.004	81.64s ± 0.38	51.11m ± 0.01
R6	13.776o ± 0.021	2.480s ± 0.010	10.770kl ± 0.036	73.067b ± 0.061	1.365r ± 0.005	89.95r ± 0.04	57.97k ± 0.05
R7	13.086r ± 0.007	57.700b ± 0.020	14.207ghi ± 0.005	20.400q ± 0.010	14.447a ± 0.031	147.00l ± 0.02	70.61j ± 0.02
P_value	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Permissible limits [123]**.**	50	200	100	100	50	2000	20

Table 7.Correlation matrix in soil metalloids, heavy metals and physic-chemical properties in polluted mine

Parameters	Pb(mg/kg)	Zn(mg/kg)	Cu(mg/kg)	Cr(mg/kg)	Ni(mg/kg)	Mn(mg/kg)	As(mg/kg)	pHwater	Org.C(%)	CEC(Cmol(+)/kg)
Pb(mg/kg)	1									
Zn(mg/kg)	0.47	1								
Cu(mg/kg)	0.88	0.53	1							
Cr(mg/kg)	0.54	0.39	0.6	1						
Ni(mg/kg)	0.6	0.46	0.5	0.07	1					
Mn(mg/kg)	0.6	0.26	0.48	0.17	0.58	1				
As(mg/kg)	0.68	0.07	0.72	0.25	0.49	0.61	1			
pHwater	0.36	0.17	0.12	0.36	0.19	0.27	-0.02	1		
Org.C(%)	0.3	-0.34	0.11	0.04	0.13	0.47	-0.03	0.15	1	
CEC(Cmol(+)/kg)	0.39	-0.12	0.1	-0.05	0.35	0.49	-0.06	0.33	0.86	1

4.1.3. Concentrations of metalloids and heavy metals in sweet potatoes (Roots, Stem and leaves) grown in contaminated mine areas

The dataset (Table 8) presents levels of various heavy metals and metalloids in sweet potato tissues (tubers, stems, and leaves) collected from five distinct locations (R1B, R2M, R4US, R6, and R7) near a polluted mine. This analysis examines contamination patterns and their potential implications for food safety and environmental health.

The most alarming finding is the excessive chromium (Cr) concentration in R1B tubers, averaging 318.4 mg/kg. The data reveals distinct metal partitioning patterns across plant tissues. Manganese (Mn) shows preferential accumulation in leaves, reaching 223.4 mg/kg in R2M samples. Similarly, copper (Cu) demonstrates higher concentrations in leaves (up to 17.5 mg/kg in R6) compared to tubers. Cadmium (Cd) and Zinc (Zn) were below limit of detection in sweet potato tissue samples.

Arsenic (As) exhibits concerning levels in specific samples, particularly in R4US stems (approximately 152.5 mg/kg) and R6 leaves (approximately 107.8 mg/kg).The sample (R1B) is marked by significant chromium contamination in tubers and high nickel concentrations. Sample (R2M) exhibits considerable manganese accumulation in all tissues, especially in the leaves. Sample (R4US) is noted for its extremely high arsenic levels in the stems. Sample (R6) is recognized for elevated arsenic and copper concentrations in the leaves. Finally, sample (R7) generally displays lower levels of contamination across most metals.

Table 8.Concentrations of metalloids and heavy metals in sweet potatoes (Roots, Stem and leaves) grown in contaminated mining areas

Sample_name	Location	Pb(mg/kg)	Cu(mg/kg)	Cr(mg/kg)	Ni(mg/kg)	Mn(mg/kg)	As(mg/kg)
Stems	R1B	<LOD	7.751 ± 0.002	3.803 ± 0.021	0.000 ± 0.000	12.843 ± 0.006	<LOD
Stems	R2M	<LOD	9.162 ± 0.002	1.325 ± 0.009	4.251 ± 0.001	43.273 ± 0.006	28.77 ± 0.02
Stems	R4US	<LOD	10.290 ± 0.010	<LOD	0.000 ± 0.000	25.153 ± 0.012	152.50 ± 0.53
Stems	R6	2.303 ± 0.006	10.190 ± 0.010	<LOD	3.713 ± 0.003	20.217 ± 0.012	<LOD
Stems	R7	0.690 ± 0.001	3.461 ± 0.002	6.717 ± 0.011	1.581 ± 0.002	9.117 ± 0.006	23.75 ± 0.01
Tubers	R1B	2.017 ± 0.012	3.413 ± 0.006	318.400 ± 0.100	18.230 ± 0.017	7.060 ± 0.002	<LOD
Tubers	R2M	0.553 ± 0.006	5.617 ± 0.021	35.747 ± 0.055	4.520 ± 0.010	33.583 ± 0.025	<LOD
Tubers	R4US	0.910 ± 0.010	3.692 ± 0.002	31.700 ± 0.020	1.153 ± 0.006	9.583 ± 0.006	<LOD
Tubers	R6	<LOD	1.837 ± 0.006	40.217 ± 0.012	0.000 ± 0.000	8.820 ± 0.010	<LOD
Tubers	R7	0.027 ± 0.006	2.751 ± 0.002	54.210 ± 0.017	0.587 ± 0.006	5.181 ± 0.001	<LOD
leaves	R1B	0.151 ± 0.001	7.513 ± 0.006	3.320 ± 0.010	4.244 ± 0.005	49.653 ± 0.025	<LOD
leaves	R2M	2.253 ± 0.011	15.597 ± 0.015	8.283 ± 0.006	2.136 ± 0.001	223.400 ± 0.100	<LOD
leaves	R4US	<LOD	6.821 ± 0.002	2.147 ± 0.012	5.271 ± 0.002	85.727 ± 0.012	<LOD

leaves	R6	1.680 ± 0.010	17.493 ± 0.015	7.827 ± 0.012	6.452 ± 0.002	137.103 ± 0.006	107.83 ± 0.06
leaves	R7	1.117 ± 0.012	3.547 ± 0.012	5.907 ± 0.006	2.352 ± 0.002	35.313 ± 0.006	<LOD
P_value		<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Permissible limits [124]**.**		0.1	40	2.3	5	500	0.1

4.1.4. Concentrations of metalloids and heavy metals in cassava (Roots, Stem and leaves) grown in contaminated mining sites

This dataset examines heavy metal and metalloid levels in cassava plants (roots, stems, and leaves) from five locations near a polluted mine as illustrated in table9: R1M, R1B, R2T, R3US, and R5. This study examines contamination patterns in cassava and compares them to previously analyzed sweet potato data. Notably, chromium (Cr) is found at concerning levels, especially in cassava roots at R1B (average 45.56 mg/kg). Manganese (Mn) exhibits significant accumulation in leaves across all locations, with the highest concentration recorded in the leaves of R1M (approximately 318.4 mg/kg). In this research the Cadmium (Cd) was below limit of detection

At R1B, elevated levels of Cr are observed in both roots (45.56 mg/kg) and stems (18.57 mg/kg). R2T shows substantial Cr in leaves (33.58 mg/kg) along with high copper (Cu) content. R3US has notable Cr levels in stems (31.11 mg/kg), while R5 shows the most alarming arsenic (As) concentration in roots (80.98 mg/kg).

In comparison to sweet potatoes, which exhibited extreme Cr accumulation in tubers at R1B (318.4 mg/kg), cassava displays moderate Cr levels in roots. Arsenic contamination is significant in cassava roots from R5, whereas sweet potatoes primarily show As in stems and leaves. Both crops indicate a preference for Mn accumulation in leaves, with cassava reaching higher maximum concentrations (318.4 mg/kg in R1M) compared to sweet potatoes (223.4 mg/kg in R2M).

Table 9.Concentrations of metalloids and heavy metals in cassava (Roots, Stem and leaves) grown in contaminated mine sites

Sample_name	Location	Pb(mg/kg)	Zn(mg/kg)	Cu(mg/kg)	Cr(mg/kg)	Ni(mg/kg)	Mn(mg/kg)	As(mg/kg)
Leave	R1B	1.080 ± 0.010	<LOD	10.077 ± 0.042	0.043 ± 0.006	3.707 ± 0.006	155.300 ± 0.346	<LOD
Leave	R1M	0.067 ± 0.006	22.717 ± 0.032	4.280 ± 0.010	<LOD	1.420 ± 0.010	318.433 ± 0.416	<LOD
Leave	R2T	<LOD	<LOD	11.073 ± 0.006	33.580 ± 0.010	3.380 ± 0.010	138.667 ± 0.208	<LOD
Leave	R3US	0.413 ± 0.006	1.441 ± 0.004	6.530 ± 0.020	2.490 ± 0.020	1.783 ± 0.015	105.367 ± 0.115	<LOD
Leave	R5	1.550 ± 0.010	<LOD	5.280 ± 0.020	4.037 ± 0.006	<LOD	104.167 ± 0.058	<LOD
Root	R1B	<LOD	<LOD	1.930 ± 0.020	45.563 ± 0.038	2.353 ± 0.006	5.120 ± 0.017	<LOD
Root	R1M	<LOD	<LOD	2.301 ± 0.001	6.287 ± 0.006	2.520 ± 0.017	15.333 ± 0.015	<LOD
Root	R2T	0.201 ± 0.001	<LOD	2.040 ± 0.030	17.170 ± 0.036	3.363 ± 0.006	10.493 ± 0.012	<LOD
Root	R3US	<LOD	<LOD	2.513 ± 0.015	26.793 ± 0.015	2.147 ± 0.006	4.663 ± 0.015	<LOD
Root	R5	<LOD	<LOD	1.777 ± 0.025	14.900 ± 0.020	<LOD	7.387 ± 0.025	80.983 ± 0.210
Stem	R1B	<LOD	<LOD	3.847 ±	18.567 ±	<LOD	75.620 ±	<LOD

				0.057	0.153		0.026	
Stem	R1M	<LOD	7.317 ± 0.021	4.253 ± 0.025	0.177 ± 0.006	1.257 ± 0.012	144.733 ± 0.115	129.133 ± 0.611
Stem	R2T	<LOD	<LOD	3.723 ± 0.051	5.253 ± 0.015	<LOD	45.897 ± 0.029	<LOD
Stem	R3US	0.600 ± 0.010	<LOD	7.383 ± 0.031	31.107 ± 0.015	5.02 ± 0.01	36.917 ± 0.021	<LOD
Stem	R5	0.463 ± 0.015	<LOD	3.000 ± 0.040	1.127 ± 0.006	<LOD	33.720 ± 0.010	<LOD
P_value		<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Permissible limit [124]**.**		0.1	100	40	2.3	5	500	0.1

4.1.5. Bioconcentration factor for Sweet potato grown in contaminated mining areas

The bioconcentration factor (BCF) for sweet potatoes grown in contaminated mining areas was assessed for multiple heavy metals: lead (Pb), manganese (Mn), chromium (Cr), nickel (Ni), copper (Cu), and arsenic (As). Samples were collected from various sites (R1B, R2M, R4US, R6, R7), representing different contamination levels and soil conditions. Table 10 presents the bioconcentration factors for sweet potatoes cultivated in these polluted mining areas.

In the tubers, BCF values were notably high for chromium (19.493 in R1B) and nickel (14.787 in R2M), indicating significant accumulation in the edible parts (see Table 10). The stems showed varied BCF results, with some locations indicating no accumulation of certain metals, highlighting that different plant parts absorb heavy metals differently. Leaves typically exhibited lower BCF values compared to tubers, although some locations recorded higher values, suggesting that metals can be transported from the roots to the leaves.

Table 10.Bioconcentration factor for sweet potatoes grown in contaminated mining areas

Sample_name	Location	BCF/Pb	BCF/Cu	BCF/Cr	BCF/Ni	BCF/Mn	BCF/As
Tubers	R1B	0.187	0.209	19.493	7.751	0.060	NA
Tubers	R2M	0.089	3.145	5.210	14.787	0.211	0
Tubers	R4US	0.053	0.156	1.063	0.263	0.092	0
Tubers	R6	0	0.171	0.550	0	0.098	0
Tubers	R7	0.002	0.194	2.657	0.041	0.035	0
Stem	R1B	0	1.293	0.233	0	0.109	0
Stem	R2M	0	3.145	0.193	13.907	0.272	1.496
Stem	R4US	0	0.434	0	0	0.240	1.521
Stem	R6	0.167	0.171	0	2.721	0.225	0
Stem	R7	0.053	0.244	0.329	0.109	0.062	0.336
Leaves	R1B	0.014	1.253	0.203	1.805	0.421	0
Leaves	R2M	0.362	8.733	1.207	6.988	1.404	0
Leaves	R4US	0	0.288	0.072	1.204	0.819	0
Leaves	R6	0.122	1.624	0.107	4.728	1.524	1.860
Leaves	R7	0.085	0.250	0.290	0.163	0.240	0

4.1.6. Bioconcentration factor for cassava grown in contaminated mining areas

The bioconcentration factors (BCF) for cassava grown in contaminated mining sites shed light on the deposition of heavy metals in various plant sections. The bioconcentration factor (BCF) values (Table 11) were assessed for elements such as lead (Pb), zinc (Zn), copper (Cu), chromium (Cr), nickel (Ni), manganese (Mn), and arsenic (As). The results of BCF tabulated in Table 11 revealed that roots showed limited accumulation for lead and zinc, with notable BCF values for chromium (up to 2.79 in R1B) and nickel (1.94 in R2T). This indicates that while some metals are absorbed, the root system may act as a barrier for certain contaminants. The stems displayed variable BCF values, with higher concentrations of manganese and copper. For example, R1M showed a significant BCF for zinc (1.227) and copper (0.568), indicating that stems can facilitate the transport of metals.Leaves had the highest accumulation of metals, particularly zinc (3.81 in R1M) and manganese (9.005 in R2T). This indicates that leaves are essential for the movement of heavy metals present in the plant.

Table 11.Bioconcentration factor for cassava grown in contaminated mining areas

Sample_Name	Location	BCF(Pb)	BCF(Zn)	BCF(Cu)	BCF(Cr)	BCF(Ni)	BCF(Mn)	BCF(As)
Root	R1B	0	0	0.322	2.790	1.001	0.043	NA
Root	R1M	0	0	0.307	0.183	1.863	0.115	0
Root	R2T	0.019	0	0.193	0.796	1.940	0.681	0
Root	R3US	0	0	0.219	0.932	0.725	0.061	NA
Root	R5	0	0	0.083	0.194	0	0.090	1.584
Stem	R1B	0	0	0.642	1.137	0	0.641	NA
Stem	R1M	0	1.227	0.568	0.005	0.929	1.087	1.535
Stem	R2T	0	0	0.353	0.244	0	2.980	0
Stem	R3US	0.045	0	0.644	1.082	1.695	0.482	0
Stem	R5	0.034	0	0.141	0.015	0	0.413	NA
Leave	R1B	0.100	0	1.681	0.003	1.576	1.317	NA
Leave	R1M	0.007	3.810	0.572	0	1.050	2.391	0
Leave	R2T	0	0	1.050	1.558	1.950	9.005	0
Leave	R3US	0.031	3.234	0.570	0.087	0.602	1.375	0
Leave	R5	0.114	0	0.248	0.053	0	1.276	NA

4.1.7. Concentration of metalloids and heavy metals in surface water near the mining site

The most notable contaminant found in the wastewater samples as indicated in Table12 is arsenic, with concentrations varying from below detection limits at certain sites to 1.675 mg/L in the "Wastewater storage in farmer field". Lead levels in the wastewater are generally low, ranging from undetectable amounts to 0.0129 mg/L in the "Processing first washing wastewater".

Copper is consistently found in all samples, with concentrations varying between 0.027 and 0.0305 mg/L. Manganese levels vary between 0.0048 and 0.109 mg/L, with the highest concentrations found in the "Wastewater storage in farmer field." Nickel was present in only a few samples, with values between 0.0017 and 0.0022 mg/L. Arsenic exhibits high mobility, with concentrations increasing from the tailings wastewater (0.392 mg/L) to downstream sites, peaking at the farmer's field storage (1.675 mg/L). Its presence in the middle reach of the Kadiridimba River (1.509 mg/L), where it is absent in both upstream and downstream samples, indicates a significant point source from mining activities. Additionally, there is a notable reduction in lead concentration from processing wastewater (0.0126 mg/L) to downstream river samples (0.0003 mg/L). The pH levels of the wastewater samples range from slightly acidic (5.49 in "Gahengeri washing wastewater") to neutral (7.09 in "Wastewater Pond under processing plant"). Several heavy elements, including zinc (Zn), cadmium (Cd), and chromium (Cr), were below the detection limit in the effluent.

Electrical conductivity (EC) values range from 64.1 to 327.1 µS/cm and total dissolved solids (TDS) values between 29.2 to 167.8 mg/L. These measurements show a progressive increase from the tailings area to downstream river sampling points, indicating a cumulative release of minerals as the water flows through the mining site and into natural waterways.

The correlation analysis of wastewater which is illustrated in table 13 revealed distinctly different heavy metal association patterns compared to the general soil contamination analysis. Lead-arsenic correlation ($r = 0.46$) was the strongest inter-metal relationship observed in wastewater samples. Interestingly, several negative correlations were observed among heavy metals in wastewater samples. Nickel exhibited negative correlations with lead ($r = -0.45$), copper ($r = -0.38$), and arsenic ($r = -0.39$). Notably the analysis revealed also strong correlations between conventional wastewater quality parameters. pH demonstrated very strong positive correlations with both electrical conductivity (EC) ($r = 0.92$) and total dissolved solids (TDS) ($r = 0.92$), while electrical conductivity and TDS showed an almost perfect correlation ($r = 0.97$).

The relationship between pH and heavy metals in wastewater differed significantly from soil patterns. Copper displayed a moderate positive correlation with pH (r = 0.28), while nickel exhibited a negative correlation (r = -0.31). Electrical conductivity showed moderate positive correlations with copper (r = 0.50) but negative correlations with nickel (r = -0.43) and manganese (r = -0.38).

Table 12.Level of metalloids and heavy metals in surface water near the mining site

Sample_name	Pb(mg/l)	Cu(mg/l)	Ni(mg/l)	Mn(mg/l)	As(mg/l)	pHwater	Ec(µS/Cm)	TDS(mg/l)
Gahengeritailling wastewater	<LOD	0.0272d ± 0.0003	0.0173a ± 0.0006	0.0049g ± 0.0001	0.3919f ± 0.0002	5.99f ± 0.01	89.17h ± 0.06	44.20h ± 0.10
Gahengeri washing wastewater	0.0016d ± 0.0001	0.0281bc ± 0.0002	<LOD	0.0870b ± 0.0010	<LOD	5.49g ± 0.01	64.20i ± 0.10	29.27i ± 0.06
Processing first washing wastewater	0.0126a ± 0.0003	0.0276cd ± 0.0001	<LOD	0.0412c ± 0.0001	1.1053c ± 0.0006	6.11e ± 0.01	161.10g ± 0.10	85.03g ± 0.06
Wastewater after washing	0.0062c ± 0.0001	0.0284b ± 0.0001	<LOD	0.0216d ± 0.0001	0.4391e ± 0.0001	6.21d ± 0.01	178.03f ± 0.06	101.77f ± 0.15
Wastewater storage in farmer field	0.0007e ± 0.0001	0.0282b ± 0.0002	<LOD	0.1054a ± 0.0039	1.6750a ± 0.0020	6.94b ± 0.05	226.97e ± 0.06	117.80e ± 0.17
Wastewater Pond under processing plant	0.0115b± 0.0004	0.0272d ± 0.0001	<LOD	0.0091f ± 0.0001	0.7196d ± 0.0001	7.05a ± 0.04	281.10d ± 0.17	140.13c ± 0.15
Kadiridimba river middle	0.0127a ± 0.0002	0.0303a ± 0.0002	<LOD	0.0163e ± 0.0001	1.5083b ± 0.0006	6.86c ± 0.01	326.03b ± 0.06	133.70d ± 0.10
Kadiridimba river	<LOD	0.0283b ±	<LOD	0.0131e ±	<LOD	6.92bc ±	324.93c ±	160.10b ± 0.26

Upstream		0.0001		0.0001		0.02	0.12	
Kadiridimba river Downstream	0.0003e ± 0.0001	0.0286b ± 0.0002	0.0021b ± 0.0001	0.0162e ± 0.0003	<LOD	6.90bc ± 0.01	327.03a ± 0.06	167.60a ± 0.17
P_value	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Permissible limits [125]**.**	0.01	2	0.07	0.1	0.01	6.5-8.5	1000	1000

Table 13.Correlation matrix for metalloids and heavy metals in surface water near the mining site

Parameter	**Pb(mg/kg)**	**Cu(mg/kg)**	**Ni(mg/kg)**	**Mn(mg/kg)**	**As(mg/kg)**	**pH(mg/kg)**	**Ec(µS/Cm)**	**TDS(mg/kg)**
Pb(mg/kg)	1							
Cu(mg/kg)	0.19	1						
Ni(mg/kg)	-0.45	-0.38	1					
Mn(mg/kg)	-0.25	-0.02	-0.34	1				
As(mg/kg)	0.46	0.28	-0.39	0.32	1			
pHwater	0.12	0.28	-0.31	-0.26	0.32	1		
Ec(µS/Cm)	0.18	0.5	-0.43	-0.38	0.15	0.92	1	
TDS(mg/kg)	0.1	0.36	-0.45	-0.36	0.08	0.92	0.97	1

4.1.8. Efficiency of papaya peel adsorbents to remove arsenic (As) in wastewater

The analysis of FTIR peaks for papaya peels revealed several important characteristics that define their chemical composition. The O-H stretching band, noted within the range of 3200-3600 cm^{-1}, showing a peak at 3301.5 cm^{-1} for the powder (see Figure 2) and 3875.7 cm^{-1} for the ash, indicating the presence of hydroxyl groups. Additionally, the C-H stretching peak, ranging from 2800-3000 cm^{-1}, showed a value of 2922.6 cm^{-1} in the powder, while the ash displayed a lower peak at 2166.7 cm^{-1} (see Figure 3), suggesting a significant presence of hydrocarbons. Moreover, the C=O stretching peak at 1609.98 cm^{-1} in the powder indicates the existence of carbonyl compounds, whereas the absence of this peak in the ash suggests that thermal degradation impacts the chemical structure.

The data in Table 14 shows a relationship between the adsorbent dose (g/L) and the effectiveness of arsenic removal. Arsenic dosage increases from 0 g/L to 3 g/L, the efficiency of removal increases from 0% to 80.08%, while arsenic concentration decreases from 1.052 mg/kg to 0.21 mg/kg. This illustrates clear dose-response relationship, with approximately 20.75% removal at 0.5 g/L, which increases to nearly 80.08% at 3 g/L(Figure 4). The results suggest that the adsorbent is effective; however, the efficiency gains diminish at higher doses. For instance, the increase in efficiency from 2.5 g/L to 3 g/L (around 10.5%) is less significant than the gain from 2 g/L to 2.5 g/L (approximately 9.4%).

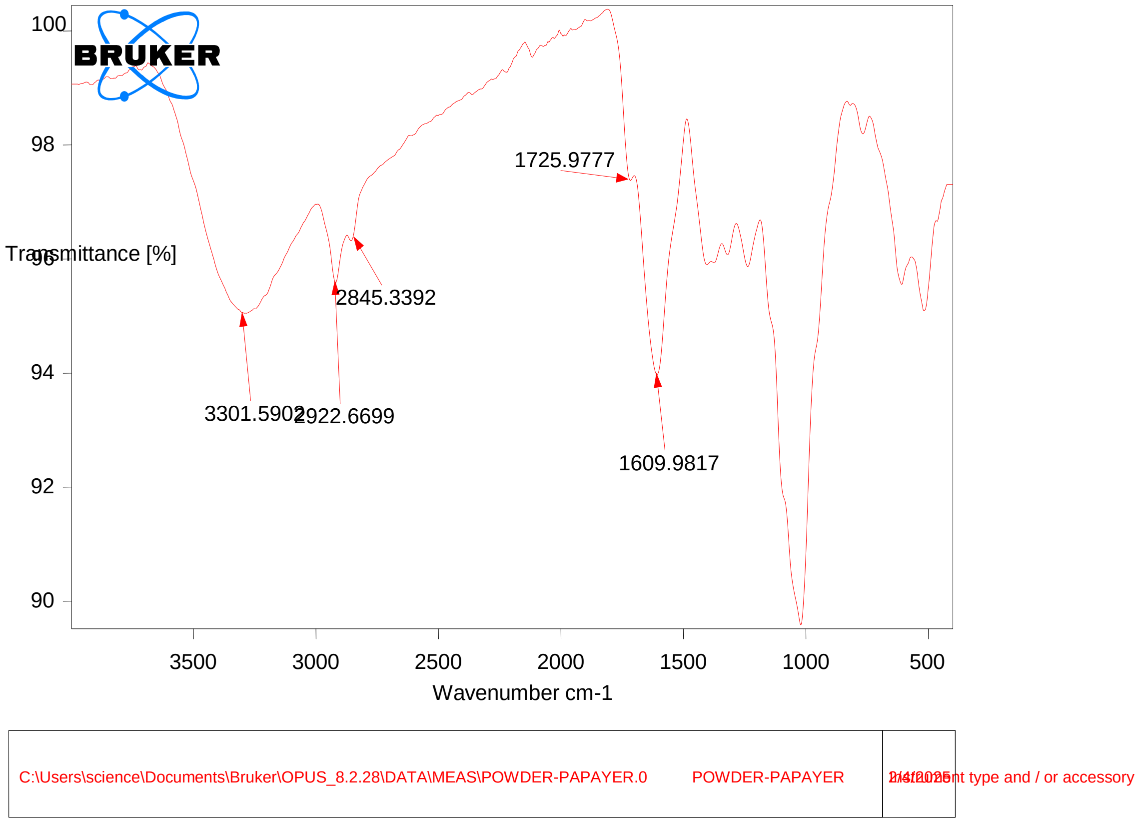

Figure 2.FT-IR of papaya peel powder characterization.

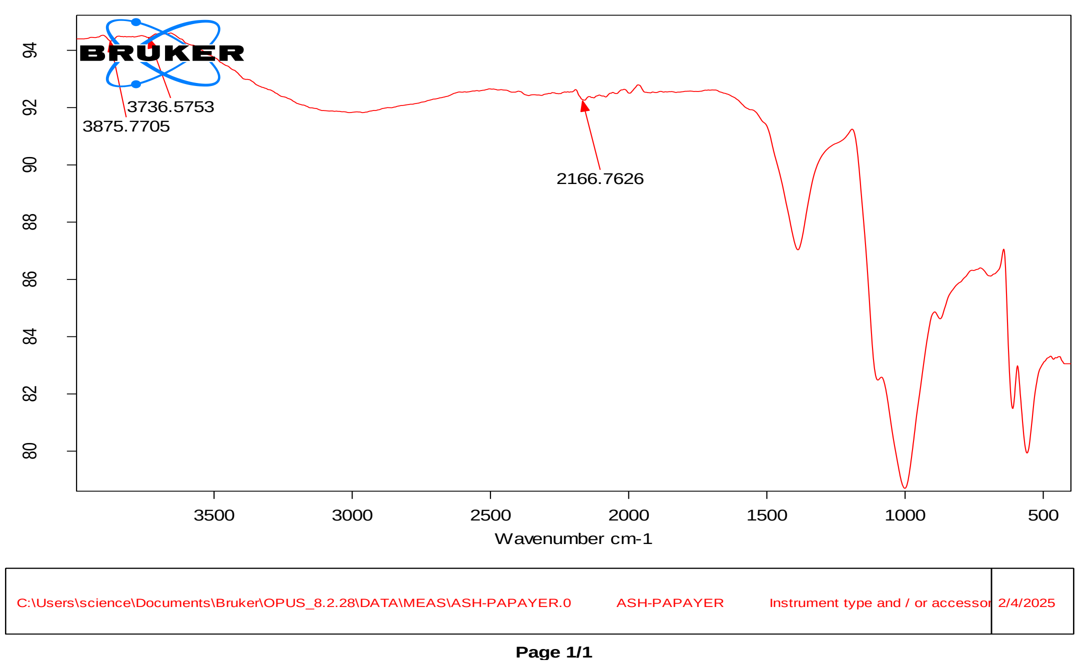

Figure 3.FT-IR of papaya peel ash characterization.

Table 14.Removal of arsenic (As) in wastewater by papaya peels

Adsorbent dosage (g/L)	As(mg/kg)	Removal efficiency (%)
0	1.052a ± 0.004	0.00e ± 0.00
0.5	0.834b ± 0.006	20.75d ± 0.57
1	0.631c ± 0.007	39.98c ± 0.44
2	0.420d ± 0.007	60.12b ± 0.68
2.5	0.320de ± 0.009	69.56ab ± 0.84
3	0.210e ± 0.009	80.08a ± 0.82
P_value	< 0.001	< 0.001

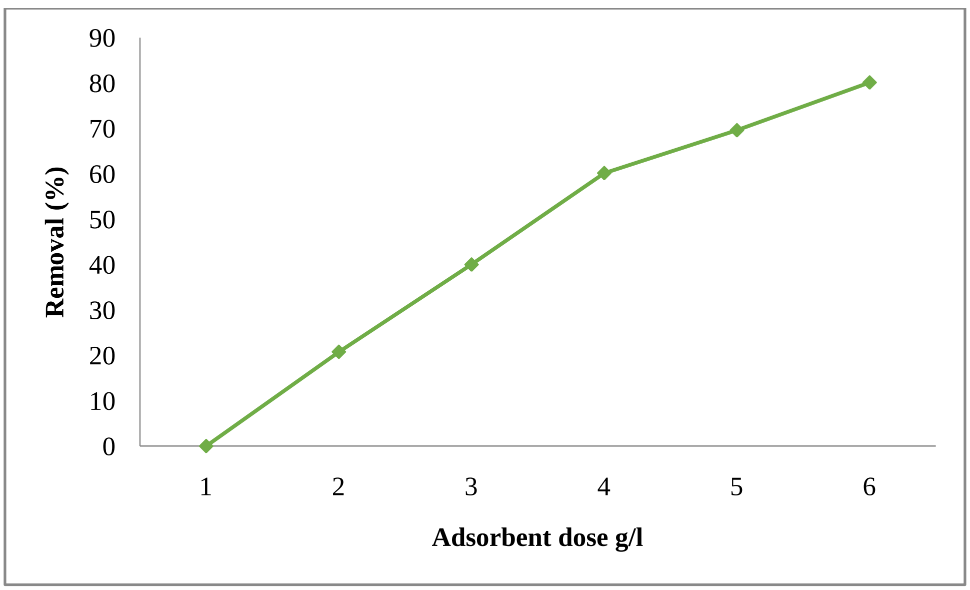

Figure 4. Removal of arsenic in wastewater using papaya peels.

4.2. Result discussion

4.2.1. Soil chemical and physical properties in polluted mine areas

The mining soils often have acidic to slightly acidic pH due to the oxidation of sulfide minerals [126]. Acidic conditions in mining-affected soils can increase the movement of heavy metals, potentially enhancing their availability and harmfulness [82]. The relatively low pH at site R2 Top (pH ~4.47) is particularly concerning, which indicated that metal solubility increases dramatically below pH 5.5 [43]. The moderately acidic pH at most sites suggests that lime application might be beneficial to reduce metal mobility, as recommended for similar mining-impacted soils [71]. In all sites Electrical conductivity are low comparing to standards. The mine tailings typically have very low organic matter content, limiting their ability to support vegetation growth[127]. Site M8 shows the highest organic carbon content (~3.33%), which could indicate either partial remediation efforts or natural accumulation of organic matter over time.CEC values show a strong positive correlation with organic carbon content across all sites ($r = 0.89$, $p < 0.001$), which aligns with established soil science principles [128]. The tailings sites exhibit very low CEC values (1.3-3.3 cmol/kg), limiting their ability to retain nutrients and buffer against changes in soil chemistry. Low CEC in mining-affected soils reduces their capacity to immobilize potentially toxic elements [129].Calcium dominates the exchangeable cation composition across all sites, followed by magnesium, potassium, and sodium. This pattern is typical of most soil types [130]. The high sodium content at sites M8 and M9 (>250 mg/kg) is concerning, as elevated sodium can deteriorate soil structure and adversely affect plant growth [131]. These sodium levels exceed those typically found in non-saline soils below 100 mg/kg [132].

4.2.2. Level of soil metalloids and heavy metals in polluted mine sites

The background Pb concentration in uncontaminated soils ranges from 10-50 mg/kg [82], suggesting that most sites in this study fall within this range. However, the considerably higher concentrations at tailing sites are due to the mineralogy of the ore. The accumulation of Pb in mining soils has been extensively documented and noted that mine tailings often contain elevated Pb levels due to the processing of sulfide ores [26]. Even though the lead (Pb) levels found in the present study are less than those found in mining sites that are extremely contaminated (>1000 mg/kg) [65], they still present potential ecological risks, particularly at sites B and C2. The average background concentration of Zn in soils is approximately 50-100 mg/kg [43], indicating that site M6 exceeds this threshold. The high Zn levels at M6 could be attributed to the specific mineralogy of the ore body or processing methods employed at this location. Zn mobility in soils is strongly influenced by pH, with greater mobility occurring in acidic conditions [43]. Given the slightly acidic nature of most sites in this study (as observed in the previous dataset), there is potential for Zn leaching and subsequent environmental transport at sites with elevated concentrations. The average Cu content in uncontaminated soils is typically 20-30 mg/kg [71], suggesting that sites M14, C1, C2, and D exceed normal background levels. Cu in mining-impacted soils often forms complexes with organic matter, affecting its bioavailability and potential toxicity [133].The relatively high Cu concentrations at specific mine sites (M14) and tailings sites warrant attention, as Cu can be particularly toxic to soil microorganisms and aquatic life if mobilized through erosion or leaching [134]. The concentrations of Cr in uncontaminated soils typically range from 10-50 mg/kg[61], indicating that sites R5, R6, M6, M14, and M15 exceed these background levels.The markedly low Cr concentration at site B (pure tailing) is particularly noteworthy and may reflect the specific mineralogy of the processed ore. The typical concentration of nickel in uncontaminated soils averages between 5 and 50 mg/kg [135], suggesting that most sites in this study fall within the lower end of this range. The Mn concentrations in soils range from 20 to 3000 mg/kg [71], having an average of around 600 mg/kg, indicate that all locations in this study fall within the lower end of the normal range. Mn is often associated with Fe oxides in soils and can influence the movement and bioavailability of other metals through competitive sorption processes [136]. The relatively high Mn levels at sites M14, C2, and M8 could potentially affect the behavior of coexisting contaminants. The typical background of arsenic levels in uncontaminated soils value from 1 to 40 mg/kg[137], indicating severe contamination at tailing sites A, B, and C2, as well as at mine sites M7 and M14.The extremely high As concentration at site B (pure tailing) represents a major environmental issue and a possible public health risk, as it surpasses regulatory thresholds for soil remediation in many countries [138]. Arsenic in mining environments is often associated with arsenopyrite (FeAsS) and other sulfide minerals, which can oxidize upon exposure to air and water, releasing soluble arsenic species[31].The varying metal profiles across different site types reflect the complex interplay between original ore mineralogy, processing techniques, and post-mining weathering processes. The elevated concentrations of As, particularly at tailing sites, represent the most significant environmental concern identified in this study. Arsenic is classified as a Class I human carcinogen and can lead to various negative health effects through several exposure pathways[139]. The extremely high As levels at site B (>545 mg/kg) exceed intervention values established by many regulatory frameworks worldwide, including the Dutch Soil Quality Standards (76 mg/kg) and the Canadian Environmental Quality Guidelines (12 mg/kg) [129].While most other metal concentrations fall within ranges that are not immediately alarming from a regulatory perspective, their combined presence (metal mixtures) could have synergistic toxic effects on soil biota and potentially affect ecological succession in these disturbed environments [134]. Chemical stabilization with iron-containing amendments has proven effective in decreasing arsenic mobility in contaminated soils [133]. Phytostabilization using metal-tolerant plant species, which can reduce erosion and leaching while potentially improving soil quality over time [140].Soil capping with clean material to reduce surface exposure and minimize wind and water erosion of contaminated particles [141].

4.2.3. Metalloids and heavy metals concentration in wastewater near Rwinkwavu mine

As noted by the World Health Organization [142], the guideline value for arsenic in drinking water is 0.01 mg/L, indicating that all detectable arsenic concentrations in this study exceed this threshold by orders of magnitude. These findings showed that the comprehensive assessment of arsenic levels in natural water sources, which identified mining activities as significant point sources of arsenic contamination[31]. The elevated arsenic concentrations, particularly in water stored in a farmer's field, present serious environmental and potential public health concerns, as this water could contaminate agricultural soils and potentially enter the food chain through crop uptake [138]. The guideline for lead levels in drinking water is set at 0.01 mg/L [142], indicating that some samples exceed this threshold. Even low levels of lead exposure can lead to cumulative negative impacts on human health, especially regarding neurological development in children [143].Copper is consistently present across all samples had concentrations between 0.027 and 0.0305 mg/L. These values are below the world health organization (WHO)[142] guidelines for drinking water set at 2 mg/L and are not immediately concerning from a toxicological perspective. The recommended health limit for manganese in drinking water is set at 0.4 mg/L[142], suggesting that the observed concentrations are below levels of immediate health concern. However, the prolonged exposure to manganese through multiple pathways could potentially lead to neurological effects[144]. Nickel was detected in only a few samples and the obtained values are under the guidelines set by the WHO [142] The guideline for drinking water is set at 0.07 mg/L, which is not considered an immediate concern. Additionally, the pH of mine drainage has a significant impact on the mobility and bioavailability of heavy metals [145]. The EC and TDS values noted in this study are comparatively lower than those usually reported for acid mine drainage (which can exceed several thousand μS/cm), further supporting the conclusion that classic acid mine drainage is not a dominant process at this site [146]. Arsenic appears highly mobile, with concentrations increasing from the tailings wastewater (0.392 mg/L) to downstream locations, peaking at the farmer's field storage (1.675 mg/L). This pattern suggests ongoing dissolution and emission of arsenic (As) from solid waste products, a phenomenon well-documented in mining environments [31].The presence of arsenic in the middle reach of the Kadiridimba River (1.509 mg/L), despite being undetectable in upstream and downstream samples, strongly suggests a point source input from the mining operation. The reduction in lead concentration from processing wastewater (0.0126 mg/L) to downstream river samples (0.0003 mg/L) demonstrates natural attenuation through dilution, as one of the primary mechanisms controlling metal concentrations in mining-impacted streams[147].When compared to international wastewater discharge standards, several parameters exceed regulatory thresholds. The US Environmental Protection Agency issued rules for metal mining effluent limitation[148] establish a maximum daily discharge limit for arsenic of 0.15 mg/L, which is exceeded by multiple samples in this study. The detection of high arsenic levels in "Wastewater storage in farmer field" raises concerns about improper wastewater management and potential agricultural contamination. Arsenic accumulation in agricultural soils can lead to crop uptake and potential human exposure through the food chain[149].

4.2.4. Metalloids and heavy metals concentration in sweet potatoes cultivated in polluted mine

The most concerning finding is the extremely elevated chromium (Cr) concentration in tubers from location R1B, averaging 318.4 mg/kg. This far exceeds the typical regulatory limit of 2.3 mg/kg for chromium in food [150]. Lead (Pb) contamination varied by location, with R1B indicating the highest concentrations (2.01-2.03 mg/kg), which exceed the maximum permissible limit of 0.3 mg/kg established by WHO/FAO [151]. Non-edible plant parts showed different contamination patterns, with arsenic (As) reaching 152.7 mg/kg in R4US stems and manganese (Mn) reaching 223.3-223.5 mg/kg in R2M leaves. This pattern of differential accumulation across plant tissues aligns with research [152], who demonstrated that non-edible portions often function as biological sinks for heavy metals, sometimes protecting edible tissues.

Copper (Cu) showed increasing concentration gradients from tubers to leaves across most locations, consistent with known copper translocation mechanisms. Conversely, chromium demonstrated preferential accumulation in tubers at certain locations, particularly R1B, which contradicts some literature suggesting limited Cr mobility within plants [150]. The elevated levels of multiple toxic elements in edible tubers raise significant food safety concerns. Consumption of these contaminated sweet potatoes could contribute to chronic heavy metal exposure, potentially causing neurological, renal, and hepatic damage [153]. The co-occurrence of multiple contaminants may produce synergistic toxic effects not accounted for in single-contaminant risk assessments [154]. The values of arsenic (As) exceed normal background concentrations for plants, which typically range between 0.02 and 7 mg/kg. Regular consumption of contaminated sweet potatoes could contribute to chronic heavy metal exposure. Chronic exposure to elevated Cr levels is associated with respiratory problems, immunological alterations, and increased cancer risk. Similarly, linked dietary Pb exposure leading to neurological disorders, kidney damage, and developmental problems in children [155].

4.2.5. Metalloids and heavy metals concentration in cassava cultivated in polluted mine

Chromium (Cr) shows concerning concentrations in cassava roots, particularly at location R1B (average of 45.56 mg/kg), greatly surpassing the allowable limit of 2.3 mg/kg for root vegetables [156]. Location R5 shows alarming arsenic (As) levels in roots (approximately 80.98 mg/kg), significantly greater than the WHO allowed level of 0.1 mg/kg of food goods [157]. Mn tends to accumulate in photosynthetically active tissues. These spatial variations reflect findings [158], WHO has shown that variations in soil pH, organic matter content, and redox conditions at specific sites significantly affect the bioavailability of metals and subsequent plant uptake patterns. While sweet potatoes showed extreme Cr accumulation in tubers at R1B (318.4 mg/kg), cassava exhibits more moderate Cr levels in roots at the same location (45.56 mg/kg). Cassava roots from R5 show substantial As contamination (80.98 mg/kg), while in sweet potatoes, As was primarily detected in stems and leaves. Both crops show preferential Mn accumulation in leaves, though cassava exhibits higher maximum concentrations (318.4 mg/kg in R1M leaves) compared to sweet potatoes (223.4 mg/kg in R2M leaves). The attribute such differences to variations in root architecture and metal transport systems between plant species[159].The elevated heavy metal levels in cassava roots raise significant food safety concerns, particularly for As and Cr. Regular consumption of As-contaminated root crops is associated with increased risks of skin lesions, cardiovascular diseases, and certain cancers[160]. Similarly [161], linked dietary Cr exposure to gastrointestinal issues, immunological dysfunction, and potential carcinogenic effects.The risk assessment is further complicated by the co-occurrence of multiple contaminants.

4.2.6. Effectiveness of papaya peel adsorbents in removing arsenic (As) from wastewater

The removal efficiency increased progressively with increasing adsorbent dosage: At a concentration of 0.5 g/L, the removal rate is 20.75%. This rate increases to 39.98% at 1 g/L, 60.12% at 2 g/L, 69.56% at 2.5 g/L, and reaches 80.08% at 3 g/L. This pattern indicates that higher adsorbent concentrations provide more available binding sites for arsenic uptake, consistent with typical adsorption behavior described in biosorption studies [162]. The effectiveness of papaya peel powder can be attributed to its lignocellulosic composition, which contains functional groups, including hydroxyl, carboxyl, and amino groups, have the ability to bind metal ions through mechanisms such as complexation, ion exchange, and electrostatic attraction [163]. The occurrence of pectin and cellulose in fruit peels offers extra binding sites that facilitate the adsorption of heavy metals [164]. The high removal efficiency of papaya peel powder for arsenic can be attributed to various adsorption mechanisms. The surface of papaya peel contains various functional groups that can interact with arsenic species through different pathways. Hydroxyl groups present in cellulose and lignin can form complexes with arsenic through coordination bonding, while carboxylate groups can facilitate electrostatic interactions with positively charged arsenic species [165].

5. CONCLUSION AND RECOMMENDATION

5.1. Conclusion

Mining operations considerably elevate the concentrations of heavy metals in agricultural soils, including lead (Pb), arsenic (As), chromium (Cr), copper (Cu), nickel (Ni), manganese (Mn), and zinc (Zn).

Arsenic levels often exceed regulatory limits, raising serious health concerns. Mine drainage and processing effluents contribute additional heavy metals to irrigation systems, with variations in soil pH enhancing the mobility and bioavailability of these contaminants. Current wastewater treatment achieves approximately 80% arsenic removal, leaving 20% that could potentially enter agricultural systems. Contamination levels tend to decrease with distance from mining operations but can extend kilometers along waterways that are used for irrigation.

Both sweet potatoes and cassava exhibit preferential accumulation of manganese in their leaves, though cassava shows higher concentrations. Elevated heavy metal levels, particularly of arsenic and chromium in cassava roots, pose significant food safety risks. Consumption of these crops can lead to metal intake that exceeds WHO/FAO provisional tolerable weekly intake values, especially for lead, chromium, nickel, and arsenic. Communities dependent on these crops face increased exposure, particularly vulnerable populations such as children and pregnant women, who are particularly vulnerable to the neurological effects of lead and the developmental consequences of long-term arsenic exposure.

5.1. Recommendation

To mitigate heavy metal contamination in agriculture areas near mining operations, immediate actions should be taken to transition to crop varieties that have lower accumulation rates of harmful metals. Incorporating biochar into the soil can help immobilize metalloids and enhance overall soil health. Additionally, applying lime can help maintain soil pH levels above 6.5, which reduces the mobility of these metals. For effective water management, establishing constructed wetlands that utilize metal-accumulating plants can filter irrigation water, while implementing alternate wetting-drying irrigation techniques can further minimize metal mobilization.

It is crucial to establish buffer zones of at least 500 meters between mining activities and agricultural lands to limit exposure to contaminants. Regular monitoring should include systematic testing of soils, water, and harvested crops in communities located near mining sites, along with public disclosure of contamination levels to keep residents informed.

Mining operations should be required to use lined tailing facilities with leachate collection systems and ensure that all discharged water meets agricultural water quality standards. Financial assurance mechanisms should be established to fund necessary remediation efforts.

Furthermore, community engagement is vital; developing visual materials to illustrate safe planting distances from contamination sources and training local extension workers in soil amendment techniques can empower residents. Improving wastewater treatment systems to exceed the current 80% arsenic removal efficiency is also essential. By implementing these coordinated recommendations among agricultural extension services, environmental agencies, mining companies, and local communities, it is possible to significantly reduce human exposure to toxic metals while ensuring food security.

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