Addis Ababa University
School of Graduate Studies
Addis Ababa Institute of Technology (AAiT)
School of Chemical and Bio-Engineering

Evaluation of Sugarcane Straw Derived Biochar for the Remediation of Chromium and Nickel Contaminated Soil

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

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Addis Ababa

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ADDIS ABABA UNIVERSITY

SUGARCANE STRAW DERIVED BIOCHAR AND ASH FOR THE REMEDIATION OF CHROMIUM AND NICKEL CONTAMINATED SOIL

Submitted by :

Name	Signature	Date

Approved by :

Thesis Advisor	Signature	Date
Chair Person	Signature	Date
Internal Examiner	Signature	Date
External Examiner	Signature	Date

DECLARATION

By submitting this thesis I declare that this thesis has been composed solely by myself and that it has not been submitted, in whole or in part, in any previous application for a degree. Except where states otherwise by reference or acknowledgment, the work presented is entirely my own. Furthermore, I took reasonable care to ensure that the work is original, and, to the best of my knowledge, does not breach copyright law, and has not been taken from other sources except where such work has been cited and acknowledged within the text.

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Signature (Selam Masresha) Date

This is to certify that the above declaration made by the candidate is correct to the best of my knowledge.

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Advisor Signature (Dr. Abubeker Yimam) Date

List Of Tables

List of figures

List of figures

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ABSTRACT

Soil constitutes a crucial component of rural and urban environments. This fact is making role of heavy and trace elements in the soil system an issue of global concern. Heavy metals constitute an ill-defined group of inorganic chemical hazards, whose main source is anthropogenic activities mainly related to fabrications. This accumulation of heavy metals soils can prove toxic to the environment. The application of biochar to soil is one way of immobilizing these contaminants through sorption by exploiting the high surface area of this material among its other essential properties. This research examined the ability of sugar cane straw, an organic waste material from sugar farm, derived biochar and ash to remediate soil contaminated with heavy metals mainly Chromium and Zinc from the effluent of electroplating industry. Biochar was produced by varying the temperature from 300°C to 500°C and ash at 700°C. The highest yield (50%) was obtained at the lowest temperature (300°C). The proximate analysis showed ash content of 42.8%, ultimate analysis with carbon content of 67.18%, the Hydrogen to Carbon ratio of 0.54 and the results from FTIR analysis disclosed the organic nature of biochar. Methylene blue absorption indicated its fine surface area and pore structure which increases with severity of temperature. Biochar was mixed with soil with at a ration varying from 4%w/w to 10%w/w of soil and the response variables was determined at a time interval of 150 days, 180days and 210days. As for ash (10% w/w), the characterization was performed at incubation time of 210days. The results of pH indicated that biochar (9.24) had a notable liming capacity of acidic soil (4.8) by increasing it to 6.89 whereas ash increased it to 7.5. The immobilization capacity of biochar was found to effected mostly by the highest production temperature (500°C) which was 75.5% for Chromium and 80.5% for Nickel. In addition, ash was shown to possess an outstanding immobilization capacity of 95.5% and 90.5% for Chromium and Nickel respectively. All in all, The results from these methods showed that biochar produced from this specific biomass possesses the typical functional groups that enable it to store carbon, the appropriate pH that could remediate acidic soil, a fine amount of macro and micro nutrients that would aid plant growth.

TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURES

ABBREVIATIONS

AC – Activated Carbon

ANOVA – Analysis of Variance

ASTM – American Society of Testing Materials

BC – Biochar

BD – Bulk Density

BET – Brunauer-Emmett-Teller

CHNS-O – Carbon, Hydrogen, Nitrogen, Sulphur and Oxygen

CEC – Cation Exchange Capacity

DF – Degree of Freedom

EC – Electrical Conductivity

FTIR – Fourier transform infrared spectroscopy

GHGs – Green House Gases

GJ – Giga Joule

HM – Heavy Metals

HTT – Heating Treatment Temperature

ICP-AES – Inductively Coupled Plasma Atomic Emission Spectroscopy

ID – Internal Diameter

MB – Methylene Blue

MSW – Municipal Solid Wastes

MWhr – Megawatt Hour

pH – Power of Hydrogen

PLC – Private Limited Company

SCSBC – Sugarcane Straw Biochar

SSA – Specific Surface Area

VOCs –Volatile Organic Compounds

1. INTRODUCTION

1.1 Background

Industrialization and technical advances have led to an increase in the use of heavy metals which consequently leads to heavy metal pollution of water and soil. More specifically, Soil contamination by heavy metals (e.g., Pb, Cd, Zn, etc.) is a matter of concern worldwide as heavy metals are non degradable and accumulate in the environment, contrary to organic substances[1].Anthropogenic activities, including electroplating, smelting, mining, use of pesticides, fertilizers and sludge are responsible for these high levels of heavy metals which results in unacceptable environmental risks. Phytotoxic concentrations of contaminants, imbalanced ratios of key nutrients, the poor physical condition of contaminated soils, and low cation exchange capacity limit the establishment of vegetation preventing or restricting the ability of soil to perform its normal functions[2].

Ex situ and in situ immobilization techniques are practical approaches to remediation of metal-contaminated soils. Remediation strategies that provide in situ immobilization of contaminants rather than ex situ removal and dumping elsewhere of soils are generally more cost-effective and environmentally friendly[3]. One such organic amendment is biochar, which is an organic carbon by product that is generated during the carbonation of waste biomass in the absence of oxygen. It is the solid material produced by thermochemical decomposition of biological residues (e.g., wood, manure, crop residues, etc.), under low (gasification) or no (pyrolysis) oxygen environment[4]. Because biochars generally have a higher surface area and greater cation exchange capacity (CEC) than native soil constituents, they have been used in trials wishing to decrease the solubility and toxicity of heavy metals and organic compounds in soils[5].The properties and sorption strength of biochars have been reported to be affected by many factors, such as heating treatment temperatures (HTTs) and feedstock sources[6].

There are a wide range of technologies that are capable of making biochar products. These include slow and fast pyrolysis, carbonisation, charcoal retorts and gasification[4].In fact, research performed in the last few years has demonstrated that phytoremediation combined with biochar addition to soil can offer additional benefits, including , improving soil fertility and crop yield and sequestrating carbon to mitigate climate change and associated improvements in plant growth[7].

To ensure cost and energy effectiveness, the use of locally available biomass which is generated as waste is necessary. In Ethiopia, currently, production of cane for commercial use is limited in three areas namely Wonji-Shoa, Methara and Fincha where sugarcane plantation is harvested 5601 ha per annum, 2,777 ha per annum and 7,372 per annum [8], respectively from three farms. In this same country, Mechanical harvesting of sugarcane is preceded by pre-harvest fire. Thus, sugarcane straw is burnt before collection of sugarcane in order to facilitate the manual harvest. But This surplus material could generate electricity and co-generate biochar via slow pyrolysis process[9]. Due to the positive effect of biochar produced from sugarcane straw for soil remediation, the use of these amendments represents not only a soil remediation option but also satisfactory alternative for the beneficial reuse of wastes.

1.2 Statement of the problem

Soil contamination with heavy metals has increasingly become a serious global environmental issue in recent years. Industrial activities such as textile, energy and power, mining and smelting, coal combustion for energy purposes in large industries, agricultural practices (fertilizers and pesticides) and municipal wastes are by far the major sources of heavy metals. More specifically, in our country Ethiopia, there are several metal manufacturing companies situated around Addis Ababa**.** Due to the various activities performed at these companies for the processing of raw metals, the wastes released react with the soil making it incapable of growing healthy vegetation. This means the soil and consequently the vegetation around that area are prone to heavy metal contamination. This bioavailability of heavy metals determines the toxicity in the soil and is a potential risk in entering human food chain. In addition, the accumulation of heavy metals in agricultural soils leads to elevated uptake by crops and affects food quality and safety.

This is all a result of soils being the major sink for heavy metals released into the environment by aforementioned anthropogenic activities. Once in the soil, heavy metals are adsorbed by initial fast reactions (minutes, hours), followed by slow adsorption reactions (days, years) and are, therefore, redistributed into different chemical forms with varying bioavailability, mobility, and toxicity. Those metals are detrimental to plant growth since they are capable of decreasing crop production due to the risk of bioaccumulation and biomagnification in the food chain. There's also the risk of superficial and groundwater contamination. Most of these heavy metals do not undergo microbial or chemical degradation thereby persisting in the environment in their total concentration even after a very long time after their release.

Knowledge of the basic chemistry, environmental and associated health effects of these heavy metals is necessary in understanding their speciation, bioavailability, and remedial options. Regardless, in Ethiopia, the application of biological remediation technologies has been very limited due to lack of appropriate equipment and extensive knowledge about the technologies developed through research which worsens the problem.

In light of the above problem, this research aimed at addressing the problem by immobilizing these harmful heavy metals before reaching the stage where it is consumed by human beings. Thus, the use of biochar and ash derived from burning of sugar cane straw, which is a waste material from sugar cane farm, will be assessed for its potential for the immobilization of heavy metals from soil by retaining them on the surface of biochar and ash so their bioavailability to plants will be irreversibly avoided.

1.3 Objective

1.3.1 General objective

The aim of this study was to evaluate the soil remediating capacity of sugar cane straw derived biochar and ash by the absorption or immobilization of heavy metals from contaminated soil.

1.3.2 Specific objectives

- ✓ To pre-treat and characterize raw sugar cane straw followed by the usage of sugar cane straw for the production of biochar and ash.
- ✓ Collecting heavy metal contaminated waste water from electroplating industry and determining its heavy metal content of spiked soil together with other characterizations.
- ✓ To characterize biochar and ash that has been produced and usage of biochar and ash produced from sugarcane straw for the immobilization of heavy metals.

- ✓ To use different techniques for the measurement and analysis of heavy metal immobilized from soil to biochar and ash.
- ✓ To compare the soil remediating capacity of biochar and ash from contaminated soil.
- ✓ To analyse data and perform evaluation of the effect of process parameters on the responses.

1.4 Significance of the study

It’s a well-known fact that Ethiopia is one of the developing countries basing more than 70% of its economy on agriculture. This shows the ever increasing demand for more land that can be used for the production of healthy agricultural products. These days, there is also growing awareness of the importance of a sustainable environment in natural resource conservation as effluent from various industries is constantly contaminating soil and water in their respective area of manufacture. Thus, biochemical processes leading to soil contamination need to be elucidated.

This type of contamination reduces the amount of land suitable for agricultural purposes and contributes greatly for food shortage in the country. The use of carbonized biomass for the purpose of in situ soil remediation is one of the evolutional methods that would not only return soil to its original productive state but also help in crop production and fertility. Thus, this research could play a role in remediation of land or water that has been heavily contaminated through high effluent concentration originating from various industries that applies heavy metals in its manufacturing processes.

In addition, this research provides experimental results about the various properties of biochar, its significance in heavy metal immobilization of soil and an introduction to the soil remediation capacities of ash. This research also provides baseline information for researchers, environmental agencies and institutions aiming to perform further study on biochar, ash and soil immobilization technology.

2. LITERATURE REVIEW

2.1 Heavy Metal contamination in Soils

2.1.1 Heavy Metals

Heavy metals, mainly including the transition metals, some metalloids, lanthanides, and actinides are a member of an ill-defined or a loosely defined subset of elements that exhibit Metallic properties. So far, many different definitions have been proposed some based on density, some on atomic number or atomic weight, and some on chemical properties or toxicity [10]. Out of this wide range of heavy metals, the main threats are associated with lead, arsenic, cadmium, chromium, nickel, zinc, mercury and others. Unlike many organic pollutants, which eventually degrade to carbon dioxide and water, heavy metals will tend to accumulate in the environment, especially in lake, estuarine, or marine sediments[11]. Although it has long been known that in the right concentrations many metals are essential to life and ecosystems, chronic low exposures to metals can also lead to severe environmental and health effects. In addition, in excess, these same metals can be poisonous[12].

2.1.2 Sources of Heavy Metals in contaminated soil

There are different sources for heavy metals in the environment. These sources can be both of natural or anthropogenic origin. The natural heavy metal sources are magmatic, sedimentary, metamorphic rocks, weathering and soil formation, the rock cycle, the origin of heavy metals in surface and groundwater as well as in the atmosphere, and anthropogenic sources stemming from human activities such as industrial production and agriculture[13].

Heavy metals are mainly released into the soil by many human activities. While the main anthropogenic sources are agricultural activities, where fertilizers, animal manures, and pesticides containing heavy metals are widely used, metallurgical activities, which include mining, smelting, metal finishing, and others, energy production and transportation, microelectronic products, and finally waste disposal[14].

In general, soils at industrial sites can have distinct groups of heavy metal(loid) contaminants, which depend on the respective industries and their raw materials and products. Soils in all urban areas are generally contaminated with lead (Pb), zinc (Zn), cadmium (Cd) and copper (Cu) from traffic, paint and many other non-specific urban sources[15].These heavy metals gain entry into the human and animal food chain through crops grown on soils contaminated with them. Such soils are often used to cultivate leafy vegetables and tuber crops to meet the demands of nearby urban populations. These crops are known for their capacity to accumulate heavy metals in their edible parts[16]. Thus, The soil chemical composition and the overall toxic metal availability in soil rhizosphere play an important role in the composition of plant materials and contribute to metal contents in fruits/ vegetables[17].

Thus, this long term irrigation by using contaminated waste water or untreated or poorly treated waste water which mainly comes from industries, will lead to the accumulation of heavy metals in agricultural soils and plants.[10]. Specific to this research, the source of heavy metal contamination is the waste water that sinks to soil released from electroplating industry. Thus, this particular source will be given much emphasis.

2.1.3 Electroplating Industry

Metal plating is the process by which a uniform metallic coating is applied to the surface of a metal part by electrochemical deposition. The metal part is called the work piece and the metallic coating which is deposited on the surface of the work piece is called the plate or finish[18].This plating industry is one of the major industries which consumes and discharges large volumes of water and wastewater containing heavy metals. This effluent is very hazardous, containing heavy metals such as nickel, chromium, copper, zinc, lead and silver as well as cyanides, hydrogen sulfides, ammonia, oil and grease and suspended solids[19].

Plating is carried out in a plating bath which is a formulated aqueous solution of various chemical compounds. The solution will contain, in addition to various complex ionic species, ions of the metal to be deposited. In most cases this is a bar of the pure metal to be deposited from the bath. For example, copper, cadmium and nickel bars are used in copper, cadmium and nickel plating baths. The process consists of a sequence of chemical and electrochemical steps. Each step in the sequence consists of the solution bath into which the work is immersed and spray rinses or running water rinses[18]. Thus, Wastewater from the electroplating plant comes from the rinse waters and the batch solutions used for plating[20].The batch solutions have a high concentration of contaminants whereas the rinse waters are comparatively dilute[21].

These wastes have a pH of around 12 and before discharge they are mixed with acid water to lower the pH[22]. The wastes from plating baths include rinse waters from copper, zinc, nickel, cadmium and lead vats. These metals are present in the wastewater in ionic form and are extremely toxic. The composite plating waste may be acidic or alkaline depending on the type of baths that are used. The effluent concentrations depend on various factors such as surface area, shape of the article, thickness of the solution and drain time[20].These wastes contain organic matter which depletes the oxygen content from the water bodies and they also have inorganic matter that make the water body unfit for further use and encourage undesirable growth of plants in the water bodies. The heavy metallic ions such as chromium, nickel, zinc, lead, silver, cadmium, copper, mercury and other toxic substances like cyanide, sulphide, ammonia, chloramines, cause damage to the flora and fauna[23].

To decrease these effects of plating waste, It is necessary to neutralize any excess acidity or alkalinity in effluent. For instance, Hexavalent chromium is removed from wastes by reduction with a reducing agent and the subsequent precipitation of the resulting trivalent chromium with lime or caustic. The chromium is reduced with ferrous iron, (specifically copperas) sulfur dioxide[18].

2.1.4 Properties and Potential Risks of selected heavy metals in plating industry

The most common heavy metals found at contaminated sites, in order of abundance are Pb, Cr, As, Zn, Cd, Cu, and Hg[24].Those metals are important since they are capable of decreasing crop production due to the risk of bioaccumulation and biomagnification in the food chain. There’s also the risk of superficial and groundwater contamination[25].

These heavy metals mostly discharged from man-made sources can easily create local conditions of elevated metal presence, which could lead to disastrous effects on animals and humans. Actually, man’s exploitation of the world’s mineral resources and his technological activities tend to unearth, dislodge, and disperse chemicals and particularly metallic elements, which have recently been brought into the environment in unprecedented quantities and concentrations and at extreme rates.

Hence, Knowledge of the basic chemistry, environmental, and associated health effects of these heavy metals is necessary in understanding their speciation, bioavailability, and remedial options[25]. The properties and effect of heavy metals mostly applied in electroplating industries Chromium and Nickel will be particularly discussed.

2.1.4.1 Chromium

Chemical and Physical Characteristics of Chromium

Chromium has atom number 24 and is a member of group VI-B of the periodic table with an atom weight of 52.0, density of 7.2 $g.cm^{-3}$, and a melting point of 1857°C. There are four stable isotopes: $_{50}Cr$, $_{52}Cr$, $_{53}Cr$,and $_{54}Cr$ with the following percentages of abundance, respectively: *431%,*3.76, 9.55, and 2.38%. It is a silvery, lustrous, malleable metal, which dissolves easily in non-oxidizing mineral acids but not in cold aqua regia or in $HN0_3$, and is therefore used in corrosion-resistant alloys[13].

The sorption and precipitation of Cr(III) and oxidation of Cr(III) to Cr(VI) are important processes in soils. The sorption of Cr(III) is strong in soils, and decreases in the presence of other inorganic cations or dissolved organic ligands in the soil solution[26].Chromium has a low mobility for translocation from roots to above ground parts of plants[12].

Sources and Applications of Chromium

Chromium is used in many industrial applications. Major sources of Cr contamination include releases from electroplating processes and the disposal of Cr containing wastes[25]. Chromium steel alloys provide high corrosion resistance and good harden ability[11].The most important Cr ore is chromite, with a world production in the order of more than 9 million tons. Cr is mostly used in the manufacture of stainless steel, for refractory purposes due to its high melting point and chemical inertness, in the making of mortars and castables[13].

It is also necessary for the making of Cr chemicals, which are used in leather tanning, catalysts, pigments, drilling muds, textiles, and others. Cr is abundant in the earth's crust and ranks 21st among the elements in crustal abundance. Cr is used in a wide variety of applications, e.g. in the paper industry, chemical industry, in fertilizers, metal works and foundries, leather tanning and finishing, and power plants[13].

Ecotoxicological Effects of Chromium

Cr is an essential element in animal and human nutrition. Chromium(III) is essential for humans and Cr deficiency can have detrimental effects on the metabolism of glucose and lipids[15]. In animals, symptoms such as impaired growth, altered immune function, disturbances in aortic plaque and size, corneal lesion formation, and decrease in reproductive functions have been observed additionally[13].On the other hand, ingestion of large amounts of Cr(III) may cause health problems such as lung cancer being a carcinogen and may cause death to animals and humans if swallowed in large doses[15].

Chromium(VI) is the more toxic form of chromium and is also more mobile. Chromium(III) mobility is decreased by adsorption to clays and oxide minerals below pH 5 and low solubility above pH 5 due to the formation of $Cr(OH)_3$[27]. Chromium mobility depends on sorption characteristics of the soil, including clay content, iron oxide content, and the amount of organic matter present. Chromate and dichromate also adsorb on soil surfaces, especially iron and aluminum oxides. Chromium(III) is the dominant form of Cr at low pH (<4)[25]

Monitoring and Legislations

It is accepted that monitoring both atmosphere and biological material from exposed workers is essential. The U.S. Standards Institute listed a maximum acceptable concentration of 0.1 $mg.m^{-3}$ for chromic acid. The U.S. National Institute of Occupational Safety and Health makes a difference between non carcinogenic Cr(VI) and carcinogenic Cr(VI). The time-weighted average values at a workplace are 25 $mg\ m^{-3}$ for airborne carcinogenic chromium and 50 $mg\ m^{-3}$ for non-carcinogenic chromium[11].

As far as the concentration of Cr in soil is concerned, Riley et al.[28] has reported soil concentration ranges and regulatory guidelines for some heavy metals. Accordingly, for Cr Soil concentration range is 0.05–3.950 ($mg\ kg^{-1}$) and the regulatory limit is 100 ($mg\ kg^{-1}$).

2.4.1.2 Nickel

Chemical and Physical Character of Nickel

Nickel has atom number 28, atom weight 58.71, specific gravity of $8.9 gcm^{-3}$, and melting point of 1453°C. Elemental Ni is a silvery white, hard, malleable metal[15]. It is soluble in dilute HNO_3, slightly soluble in HC1 and H_2SO_4, and insoluble in NH_4OH.

There are five stable isotopes with the following relative abundances: $_{58}$Ni(68.27%), $_{60}$Ni (26.10%), $_{61}$Ni (1.13%), $_{62}$Ni (3.59%), and $_{64}$Ni (0.94%).

In soils, Ni occurs in several chemical forms. In the soil solution, Ni occurs in the free ionic form (i.e. Ni 2+) or complexed with organic and inorganic ligands. Ni is readily sorbed by soils at low (<10 ppm) concentrations. sorption of Ni from soils depend largely on pH[13].

Sources and Applications of Nickel

Ni ranks 23rd in crustal abundance with an average content of 80 ppm. The two most important Ni ores are pyrrhotite and pentlandite, a sulfide. Ni is mainly used for electroplating, alloy production, Ni-Cd batteries, electronic components, and catalysts for hydrogenation of fats and methanation. Nickel is a transition element with a broad range of applications in modern industry, being used in everything from coins to automobiles to jewellery. The largest Ni use by far is the manufacture of stainless steel. Moreover, Ni is an excellent catalyst for many reactions and so it is used for a large number of industrial and research applications alone or in combination with other metals[15]. Ni-steel alloys are used for armour plating and armaments as well as for turbine blades, jet engine components, and in nuclear reactors. The main sources of Ni in the environment are from mining and smelting, from sewage sludge, and from fuel oil and coal combustion[13].

Ecotoxicological Effects of Nickel

Ni is an essential nutrient for both plants and animals. Symptoms of Ni deficiency in plants are various and include growth depression, premature senescence, decreased tissue Iron levels, chlorosis, and necrosis. It is an element that occurs in the environment only at very low levels and is essential in small doses, but it can be dangerous when the maximum tolerable amounts are exceeded. This can cause various kinds of cancer on different sites within the bodies of animals, mainly of those that live near refineries[25].

There are several types of Ni poisoning in humans. Inhalation of Ni components such as leads to pneumonitis with adrenal cortical insufficiency, pulmonary oedema, and hepatic degeneration, cancer of the respiratory tract, pulmonary eosinophilia, and asthma. The most common effect of long-term Ni skin contact in humans is contact dermatitis[13].

Monitoring and Legislations

The Department of Petroleum Resources [29] in Nigeria has recommended guidelines on remediation of contaminated land based on two parameters intervention values and target values. Target values indicate the soil quality required for sustainability or expressed in terms of remedial policy the soil quality required for the full restoration of the soil's functionality for human, animal, and plant life. The target values therefore indicate the soil quality levels ultimately aimed at. Accordingly, the target value of nickel was determined to be 140.00 (mg kg^{-1}) and the intervention value is 720.0 (mg kg^{-1}).

2.1.5 Remediation Techniques of Contaminated soil

Given the potential adverse impact of pollutants on environment and human health, there has been a significant move toward developing strategies to manage contaminated sites. The management of contamination can be split into three categories: reducing inorganic concentration to an acceptable level; isolation of contamination to prevent any further reaction of the soil with the environment; and reducing the biological availability (i.e., bioavailability) of inorganic contaminants[30].

Metal(loid)-contaminated soil can be remediated by chemical, physical, or biological techniques (or a combination of all three). The technology applied is often specific to the metal(loid) contaminant to be removed and the site characteristics and may be further classified into in situ and ex situ categories. In situ *remediation* takes place on site and does not require excavation of the contaminated soil, limiting the exposure pathways to other organisms, including humans. [31].*Ex situ remediation* techniques require the excavation of polluted soil for subsequent treatment or disposal. Specific to this study, Biological techniques will be briefly introduced.

2.1.5.1 Biological Techniques

Bioremediation refers to the attenuation of metal(loid)-polluted sites by (natural) processes using organisms such as microbes or plants. Both stabilization and removal mechanisms exist within bioremediation. Unlike hydrocarbon-contaminated soils where bioremediation has been extremely successful, the use of microbes to remediate metal(loid)- contaminated soils has been limited to those elements that can be converted into gaseous forms (e.g., arsenic, mercury) or transformed into less toxic forms, an example being reduction of toxic hexavalent chromium to nontoxic trivalent chromium[31].

Phytoremediation is an emerging technology that exploits the genetic potential of selected plant species to remove, degrade, metabolize, or immobilize a wide range of contaminants[16]. Conceptually, this remediation approach treats a living plant as a solar-driven pump capable of extracting and/or concentrating particular pollutants from soil, sediment, and aqueous environments[31].

2.1.5.2 Immobilization

The immobilization or stabilization of trace elements in soil is a remediation method that reduces contaminant mobility and bioavailability through the use of soil organic and inorganic amendments to accelerate the attenuation of metal toxicity in soils [32],[26]. The mostly applied amendments include clay, cement, zeolites, minerals, phosphates, organic composts, and microbes[33]. These amendments immobilize trace elements by absorbing, complexing or (co)precipitating them in soil. Thus, the main aim to immobilize/stabilize the labile trace element fraction in soil that is, the fraction that can be easily released into soil solution, leached to groundwater and enter the biological cycle. It is a remediation technique based on the naturally occurring processes in soil; hence, it is also known as assisted natural remediation or attenuation[34].

These stabilization techniques are also more sustainable and cost-effective solution for decreasing the mobility and bioavailability of trace elements. The main purpose of in situ trace element immobilization is to aid plant establishment, recover soil micro and mezzo fauna and restore soil functions through reduced trace element mobility and bioavailability[26].This is the method used in this research by the application of biochar and ash. The details of this technique in relation to the remediating material is discussed in section 2.5.1.

2.2 Biomass

Biomass can generally be defined as any hydrocarbon matter that is derived from natural ecosystems such as forests, grasslands and aquatic ecosystems or any kind of lignocellulosic residues or the products from energy crops[35]. Common types of biomass are – crop residues, animal manure, recycled organics, paper mill waste, wood chips, tree bark, municipal green waste, bio solids, sugar mill residues, etc[36].

In addition its use for the production of biochar, biomass has a unique characteristic compared with other forms of renewable energy: it can take various forms such as liquids, gases, and solids, and so can be used for electricity or mechanical power generation and heat. If biomass could be converted into useful energy, the consumption of fossil fuel and greenhouse gas emissions would be decreased. Furthermore, the use of biomass could lead to the creation of a new biomass industry, which would help revitalize agriculture and forestry, leading to social stability as well as economic stimulus[37].

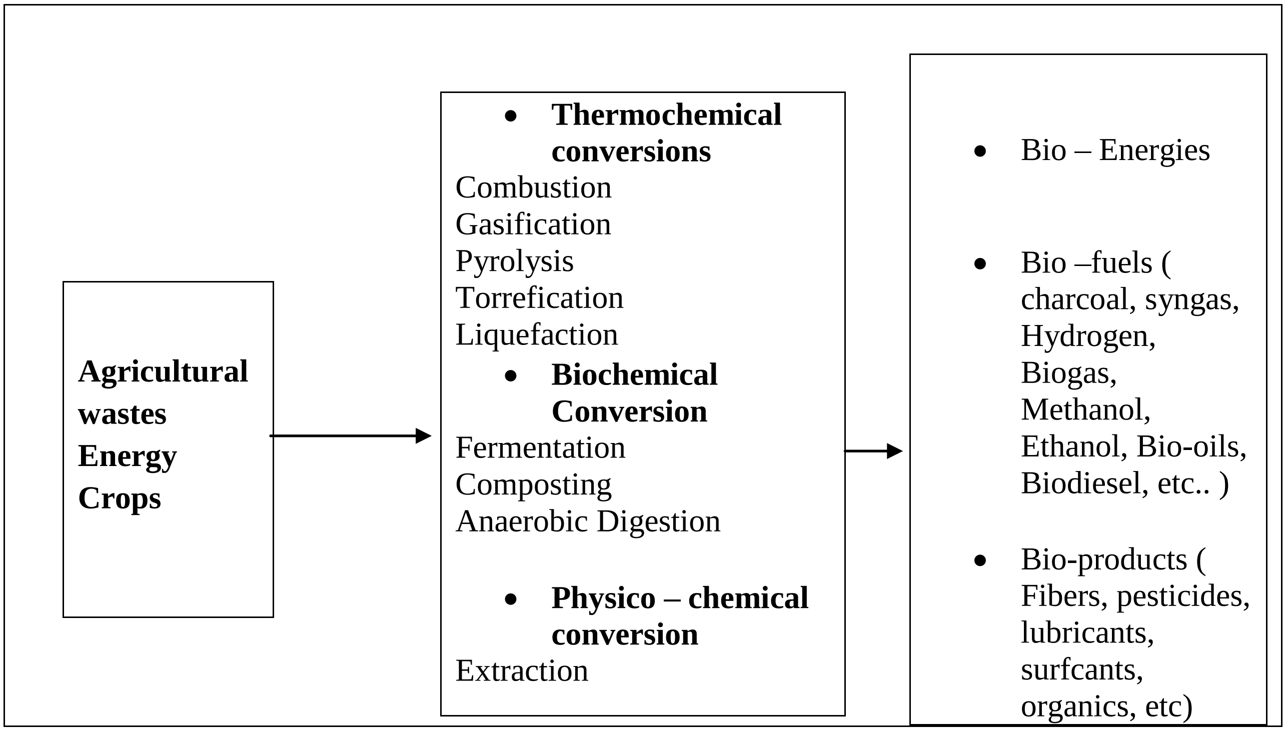


Figure 2.1: Biomass conversions for useful and valuable products (Redrawn from [38])

2.2.1 Sugarcane Straw

Sugarcane is an important crop for Ethiopian economy. Currently, there are three large-scale sugar establishments in the country; two of them in the Awash Basin (Wonji/shewa and Metehara) and one (Finchaa) in the Blue Nile Basin. The present level of national production from the three-sugar estates is about 261,041 tons of sugar and 87,257 tons of molasses per annum respectively[39].

Manual harvesting, type of harvesting used in Ethiopia, of sugarcane is an example of a current agricultural practice that uses fire. The practice of burning the sugarcane residues to facilitate harvest and transport operations has been widespread worldwide to reduce the cost of harvesting sugarcane, especially in non-mechanized operations (i.e. manual harvesting)[40]. However, this common practice of pre-harvest burning of sugarcane straw emits particulate material, greenhouse gases, and tropospheric ozone precursors to the atmosphere. Even if policies exist to eliminate the practice of pre-harvest sugarcane burning in the near future, there is still significant environmental damage[41]. The environmental damage includes affecting the health of the resident population in the vicinity, making them more susceptible to diseases, above all respiratory ones. A larger number of people can be subject to its effects in the event that the dominant winds are directed towards more densely populated areas since many urban areas are typically located next to sugarcane cultivated areas as well as ethanol and bioelectricity plants[41].

Table 2.1: Conversion of sugarcane waste into biochar and energy[9].

Feed Stock	Biochar Yield(dry basis)%	Syngsas energy produced MW/ton (dry feed)	Electricity production (MWhr/tone dry feed)
Sugarcane Straw	33.6	1.33	0.5
Bagasse	31.3	1.35	0.5

As shown in table 2.1, The sugarcane industry in many parts of the world produces food and energy (stationary and fuel). Thus, the industry is well positioned to offer greenhouse gas abatement and climate change mitigation.

The thermal conversion, via a slow pyrolysis process, of cane residues such as green harvest trash and bagasse can produce thermal or electrical energy as well as biochar. Studies have shown that a commercial slow pyrolysis unit could generate over 1 MWhr of electricity from every two tonnes of trash with a biochar recovery of between 31.3–33.6 %. Recent work has demonstrated sugarcane residues can generate energy in the form of electricity through combustion of the syngas (methane, hydrogen and carbon monoxide) in a gas Engine[4]. Thus, this surplus material could co-generate biochar via slow pyrolysis in addition to the generation of electricity biofuel.

2.3 Biochar

2.3.1 Definition

Charcoal is created both naturally as a result of vegetation fires and intentionally by humans in burn pits and hand-made structures. When charcoal is made for the purpose of adding it to soil as an amendment, it’s called biochar[42]. Biochar is a term reserved for the plant biomass derived materials contained within the black carbon continuum. This term is a relatively recent development, emerging in conjunction with soil management and Carbon sequestration issues. ‘Activated carbon’ is a term used for biochar-type substances, as well as for coal, that have been ‘activated’ in various ways using, for example, steam or chemicals. This process is intended to increase the surface area for use in industrial processes such as filtration[43].

Biochar has drawn significant attention as a soil amendment and remediation. Being a fertilizer itself, biochar has ability to absorb water and nutrients and remains moist[44]. This unique characteristics of the biochar increases its effectiveness in retaining most nutrients and keeping them available to plants than other organic matter such as for example common leaf litter, compost or manures[45]. In addition to these purported benefits to the soil, biochar consists for a large fraction out of fixed carbon (50 – 85 *w*%) which has been demonstrated to be very stable, with a half-life of over 1000 years in the soil[46].

Despite the good things that biochar can do for soils, making charcoal in the traditional method is not an environmentally friendly practice. The first evidence of charcoal made by humans being used as a soil amendment was in the Amazon Basin of South America over 2,500 years ago. Archaeological evidence suggests that ancient people piled and covered wood in earthen pits, then burned it slowly with limited air. This method, still used today in developing countries, creates considerable smoke and releases half the carbon dioxide (CO_2) in the original biomass along with other greenhouse gasses (GHG’s). That’s not healthy for people or the atmosphere and all that heat (energy) is wasted[42]. Today, biochar is produced using pyrolysis, that is, the process when organic material is turned into carbonaceous material. It is combustion of organic material with low to no access of oxygen. Through the pyrolysis organic material is turned into energy products in form of fine-grained, porous and carbon rich material, gas and oil[47].

In this modern method, volatile gases, hydrocarbons and most of the oxygen and hydrogen in the biomass are burned or driven off and captured, including GHG's. These captured emissions are known as syngas (synthesis gas) and can be used like natural gas. Liquids, called bio-oils, are also captured creating another source of energy, leaving carbon-enriched biochar[42].Thus, utilization of biochar for soil amendments is reported as a means of abating climate changes by sequestering carbon (i.e., storage in soil) while simultaneously increasing crop yields and producing energy[48]. As a carbon-rich material with various acidic and basic functional groups, biochar has also showed promising results (i.e., 2–200 mg g^{-1} adsorption capacity) in organic and inorganic contamination removal from water (e.g., phenol, methylene blue, Cu^{2+}, Cd^{3+}, Pb^{2+}, and Zn^{2+})[49].

2.3.2 Properties of Biochar

In order to make the best use of biochar, we must improve our understanding of its properties in relation to both the feedstock and the pyrolysis method used to manufacture it. It is logical that this physical feature of biochars will also be of importance to their behavior in soil processes. Thus, a primary focus was given to those characteristics that are more likely to impact on soil properties and processes when biochar is incorporated into soil.

2.3.2.1 Heavy metals content of BC

Although little research has been conducted on the possible toxic effects of biochar- amended soils, the potential effects associated with the presence of heavy metals and organic compounds condensed on the surface of biochar during pyrolysis are of concern[50]. Heavy metals present in the feedstock (e.g., MSW, sewage sludge, treated wood, etc.) are most likely to remain and concentrate in the biochar. Therefore, careful selection and analysis of feedstock is necessary to avoid contamination of biochar with increased levels of heavy metals.

Heavy metals are stable materials and therefore retained during volatilization of associated organic molecules. The majority of metals will, therefore, be present as ash within biochar (together with nutrient elements such as phosphorus and potassium). It may therefore be possible to manipulate contaminant loadings through selective removal of ash. Alternatively, it has been shown that high temperature pyrolysis can release heavy metals form the solid product, thus yielding char with lower loading of these contaminants[51].

2.3.2.2 Porosity and Surface Area measurements

These physical properties strongly affect the behavior of biochar in soils and porous media. The pore-size distribution of biochar has long been recognized as an important factor for adsorption application. Biochar pores are classified in this review into three categories according to their internal diameters (ID): macropores (ID>50 nm), mesopores (2 nm< ID <50 nm) and micropores (ID <2 nm)[52]. Each size range of pores contributes to a different property of the sample. Micropores contribute most to the surface area of biochars and are responsible for the high adsorptive capacities for molecules of small dimensions such as gases and common solvents[43].For soil applications, Macro-pores will primarily contribute to its ability to promote aeration and hydrology and even provide refuge for microbes[53]. The larger the pores, the easier water, plant roots and fungal hyphae can penetrate the particle and the more chemical interactions char can participate in per gram[54].

The most common type of analysis of surface area is a gas sorption isotherm measurement. Through this measurement, it has been discovered that biochar has a very high specific surface area (SSA) of several hundred m^2g^{-1} to a thousand $m^2g\text{-}^1$[55]. Properties of biochar are decisively affected, not only by properties of parent material, but also by operating conditions used, mainly the heating rate, the maximum temperature experienced and the residence time at this temperature[56]. Among those operating parameters, HTT is thought to be the most significant factor for the resulting pore distribution in charcoals, as the physical changes undergone by the biomass feedstock during processing are often temperature-dependent[57].

2.3.2.3 EC and Bulk Density

The density of char can be measured in two ways: bulk density, which includes structural and pore space volume, and particle density (also known as skeletal or true density), which includes only the volume occupied by solid molecules[54].Bulk density (BD) is the mass/volume of the material including intra- and inter-particle pores. This property is relevant to storage and transport, and it indicates the potential change in soil or potting soil density when biochar is added[58].

Electrical conductivity (EC) indicates the capacity to transport electricity. EC depends on the salt content of the biochar and thus could be used to calculate the salinity of the material[58].

2.3.2.4 pH

Since pH affects so many physical, chemical and biological properties of soil, being able to predict the pH effects of a biochar is critical to choosing the right char for the right application[54]. Considering the very large heterogeneity of its properties, biochar pH values are relatively homogeneous, that is to say they are largely neutral to basic. Consequently, biochar pH values from a wide variety of feedstocks and found a mean of pH 8.1 in a total range of pH 6.2 – 9.6[59]. Lower pH values in soils (greater acidity) often reduce the CEC and thereby the nutrient availability. Thus, The liming effect has been discussed in literatures as one of the most likely mechanisms behind increases in plant productivity after biochar applications[60].

2.3.2.5 Exchangeable Bases and CEC

Measurements of the content of exchangeable elements are used to check the availability of elements to plants and their nutritional balance relative to plant needs. The sum of the exchangeable elements N, P, K, Ca, and Mg is normally used to calculate the cation exchange capacity (CEC) of the soil. Biochar has the capacity to exchange cations (such as nitrogen in the form of ammonium, NH_4+) with soil solution, and thus store crop nutrients. The extent of this capacity (cation exchange capacity, CEC) is effectively absent at very low pH and increases at higher pH[61]. Large additions of biochar have been shown to increase the CEC by as much as 50% in highly weathered soils. The CEC of biochar seems to also increase as the pyrolysis temperature[51]. Experimental results show that the CEC of fresh biochar is typically very low, but increases with time as the biochar ages in the presence of oxygen and water[55].

2.3.2.6 General Properties

Data collected on the total ash, C, H, N, and S contents of the biochars in addition to the proximate analysis quantifying the amount of ash and organic materials according to ASTM Standards (D1762-84) is considered the most common analysis for attaining of biochar composition. A “good” charcoal is one that is mostly fixed carbon, with some volatiles to ease the ignition process and low moisture and ash[54]. Despite the feasibility of biochar being produced from a wide range of feedstocks under different pyrolysis conditions, its high carbon content and strongly aromatic structure are constant features. Consequently, biochar production is often assessed through changes in the elemental concentrations of C, H, O and N and associated ratios. Specifically, H/C and O/C ratios are used to measure the degree of aromaticity and maturation[47],[43]. Accordingly, these features largely account for its chemical stability[52].

Use of some form of proximate analysis is prevalent in biochar literature, though numerous researchers have questioned the relevance of proximate analysis data for soil applications. It is true "high volatile matter" chars have appeared to cause nitrogen immobilization problems in some soil but much more work is needed to make this analysis more useful for determining char quality in relation to soil application[54].

2.4 Biochar Production through Pyrolysis

The rising energy cost and concerns over greenhouse gas emissions associated with the use of fossil fuels have prompted significant research interest into the conversion of biomass into biofuels and other value-added renewable products. Among the wide array of biomass conversion technologies, pyrolysis is unique because it not only converts a large fraction of the biomass into a condensable liquid crude biofuel, called bio-oil, but additionally produces a solid fraction known as biochar[46]. In the early developments of pyrolysis, producing biochar was the sole objective of wood carbonization. Throughout history the process has evolved from using wasteful biochar pits to modern, fast pyrolysis reactors and bio-oil refineries. At the end of the eighteenth century, new technologies were developed to recover and utilize the volatile compounds produced from pyrolysis[62].

The word is derived from Greek word 'pyro' meaning fire and "lysis" meaning decomposition or breaking down into constituent parts. In practice it is not possible to create a completely oxygen free environment and as such a small amount of oxidation will always occur[52]. Pyrolysis carbonizes organic matter in the absence or in quasi absence of oxygen at temperatures between 275°C and 1000°C. The organic matter is thermo-chemically transformed, producing gases, oils, and solid residues. The oils can be used to produce energy or new products such as biopesticides[46]. Thus, Pyrolysis provides an interesting alternative to direct soil application, composting, methanization, and incineration since the gases produced are usually captured and recycled within the pyrolysis system, thus reducing GHG emissions; and the resulting material, biochar, is stabilized, making it easy to handle, transport, and distribute[58]. The heat transfer rate during pyrolysis is one of the most important parameters for determining the yield and property of products[62]. The compositions and amount of each substrate will differ depending on how the process is set up. Some of the leading parameters determine the final product are particle size, temperature and residence time in the process[63]. Specific to this research, more focus will be given to slow pyrolysis.

2.4.1 Slow Pyrolysis

This is the conventional process whereby the heating rate is kept slow (approximately 5-7°C/min). This slow pyrolysis process where lower temperature (typically 400°C) and longer vapour residence times is maintained[54]. These conditions result in increased cracking reactions that reduce the liquid organic yield and consequently increase the biochar yield[64]. Consequently, slow pyrolysis is often referred to as "carbonization" due to the relatively high proportion of carbonaceous material it produces which is biochar[52]. As The target product is generally the char, but this will always be accompanied by liquid and gas products although these are not always recovere[55]. Basically, slow pyrolysis gives rise to approximately 35 % biochar, 30 % bio-oil, and 35 % syngas by mass[65].

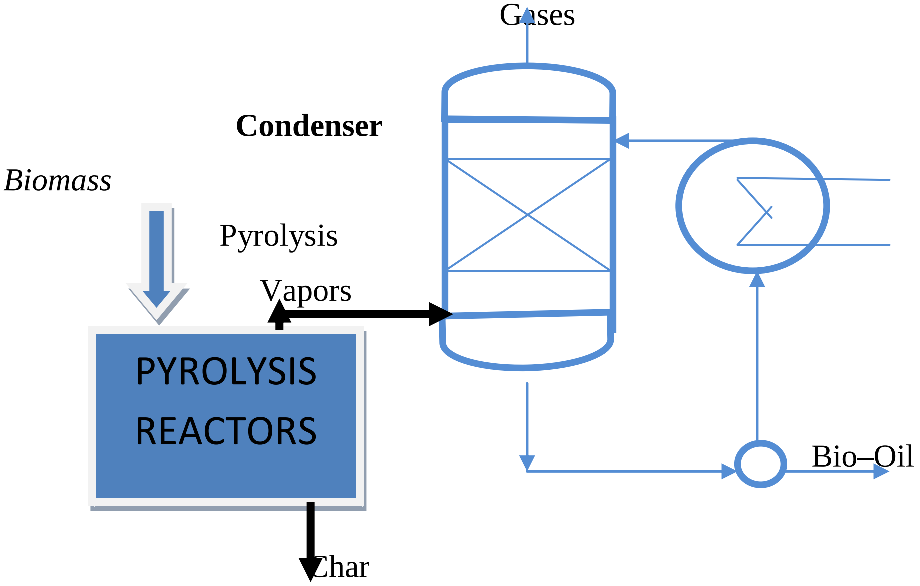


Figure 2.2: Pyrolysis scheme for the production of biochar, bio-oil and gases (Redrawn from [82])

2.4.2 Paramters in slow pyrolysis

The nature and preparation of pyrolysis feedstocks as well as the process conditions used influence both the composition and distribution of products. The main effects are caused by feedstock particle size, the heating rate and temperature control; they are summarized here in the context of slow pyrolysis which is the type used in this research.

2.4.2.1 Feedstock properties

Feedstock possessing high lignin content will tend to give higher char yields, other components leading more to liquid and gas products. Minerals present can have a catalytic effect increasing char yields in some cases[55]. It is generally assumed that an increase in particle size causes greater temperature gradients inside the particle. Due to the temperature gradient, at a given time, the temperature of the core is lower than the surface temperature. The cores of larger particles become carbonised but cannot be decomposed completely, which results in an increase in char yield but a decrease in liquids and gases. In addition, Larger particle size can increase char yields by restricting vapour disengagement and increasing the scope for secondary, char-forming reactions[55]. Smaller particles provide a greater reaction surface and a high heating rate, which allows a quicker decomposition of the biomass[35].

2.4.2.2 Temperature

Temperature control is the most important operational variable with peak temperature being most significant. Higher peak temperatures lead to lower char yields and higher liquid yields. For instance, a typical biomass pyrolysis might yield 40% biochar by weight at 350°C but only 25% when heated at 550°C. Temperature also influences the composition and structure of the biochar formed[55].

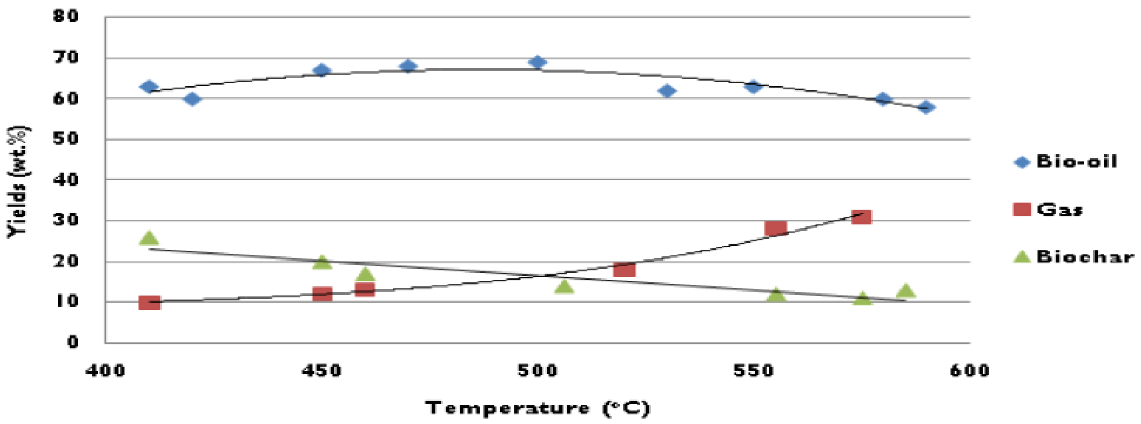


Figure 2.3: Product Yield from pyrolysis of biomass at various temperature[66]

One of the most important properties of biochar, Porosity, significantly increases between 400°C and 600°C. These increases in porosity result in significant increases in surface area by orders of magnitudes[43]. This is a result of higher temperatures and longer residence times leading to chars with higher levels of total-carbon and analytically fixed-carbon, as more volatile matter is driven off; pore structure and surface area also develop with more forcing conditions[55]. Lower temperature biochar that has been pyrolyzed between 400 and 500°C or under different moisture and pressure conditions has the chief advantage of increasing the soil (CEC). Furthermore, this biochar type sequesters soil C, however not to the same extent as high temperature biochar[65].

2.4.2.3 Heating Rate and Residence time

The relatively high flow rates of gas and relatively low residence time of biochar might be expected to produce biochars with properties distinct from biochar produced by slow pyrolysis[43]. It is recorded heating rates have a smaller and inconsistent effect in slow pyrolysis. Still, it has been observed micro-pore volume and openings are highly affected by the heating rates deducing that high heating rate chars mainly consist of macro-pores. The BET surface area and micro-pore volume increase for increasing heating rate up to 10°C/min[35, 65]. Also, Increasing residence time at peak temperature will lead to lower char yield, but again in a smaller effect[55].

2.5 Biochar and its Applications

In this section, the various applications of biochar in regards to its carbon sequestration and GHG emission mitigating capacity in addition to its ability to give soil various properties that will enhance its fertility, nutrient retention which will eventually affect its productivity will be briefly shown. As this research is mainly related to the application of biochar for the remediation of heavy metal contaminated soil, more emphasis will be given to the revision of literatures illustrating previous work done highly related to this subject.

2.5.1 Biochar for soil amendment

Biochar for Soil Fertility and Crop productivity

Many studies have reported beneficial effects of biochar as a soil amendment for improving soil quality and crop productivity. Amendment biochar can restore soil fertility and could be used to replenish soil carbon pools[67]. The incorporation of biochar into soil can alter soil physical properties such as texture, structure, pore size distribution and density with implications for soil aeration, water holding capacity, plant growth and soil workability[68]. This includes provision of labile organic matter, rapid utilization of labile substrates in soil can build a store of nutrients in soil microbial biomass, which may become available for plant acquisition and growth over time[55]. In addition, biochar has an impact on addition and nutrient retention. The ash in biochar contains plant nutrients, mostly bases such as Ca, Mg, and but also P and micronutrients including zinc and manganese [69]. Also few studies attributed the positive plant responses to other effects of biochar on nutrient availability rather than simply as a direct supplier of nutrients[43].

In the case of pH, Lower pH values in soils (greater acidity) often reduce the CEC and thereby the nutrient availability[52]. In these cases where the soil's pH is below optimal for its intended use, a rise in pH can provide wide range of benefits in terms of soil quality, notably by chemically improving availability of plant nutrients, and in some cases by reducing the availability of detrimental elements such as Aluminum[70]. Also, Surface area is a very important soil characteristic as it influences all of the essential functions for fertility, including water, air, nutrient cycling and microbial activity. The limited capacity of sandy soil to store water and plant nutrients is partly related to the relatively small surface area of its soil particles.

Indications exist that biochar will similarly change the physical nature of soil, having much of the same benefit of other organic amendments in this regard. Biochar specific surfaces, being generally higher than sand and comparable to or higher than clay, will therefore cause a net increase in the total soil-specific surface when added as an amendment. Also, Several workers have reported that biochar applications to soils have shown positive responses for net primary crop production, grain yield and dry matter. This impact of biochar application is seen most in highly degraded acidic or nutrient depleted soils[64].

By increasing the water retention capacity of a soil, biochar increases the potential for crops to retain more plant available water and thereby increasing crop yields and reducing water stress during critical periods of water restriction[54]. It is reported that, depending on the amount of biochar added, improvements in plant productivity range from 20 to 220%[71]

Biochar and heavy metal Immobilization

Biochar has been shown to be very effective in adsorbing and sequestering a number of heavy metals and trace elements including arsenic, cadmium, chromium, copper, lead, mercury, nickel and zinc, thus making it well suited to remediate soils contaminated by heavy metals. A number of studies have shown that biochar application is effective in heavy metal immobilization, thereby reducing the bioavailability and phytotoxicity of heavy metals[3],[72],[86]. The bioavailability of heavy metals determines the toxicity in the soil and potential risk in entering human food chain[73]. Sequestering the heavy metals means that the metals are no longer biologically available to plants, animals or humans, and that they are not available for transport offsite in water or air. Biochar thus reduces exposure potential to animals and plants. Reducing phytotoxicity allows soils that were once contaminated to support diverse and healthy vegetation, which is critical to restoring ecological services[74].

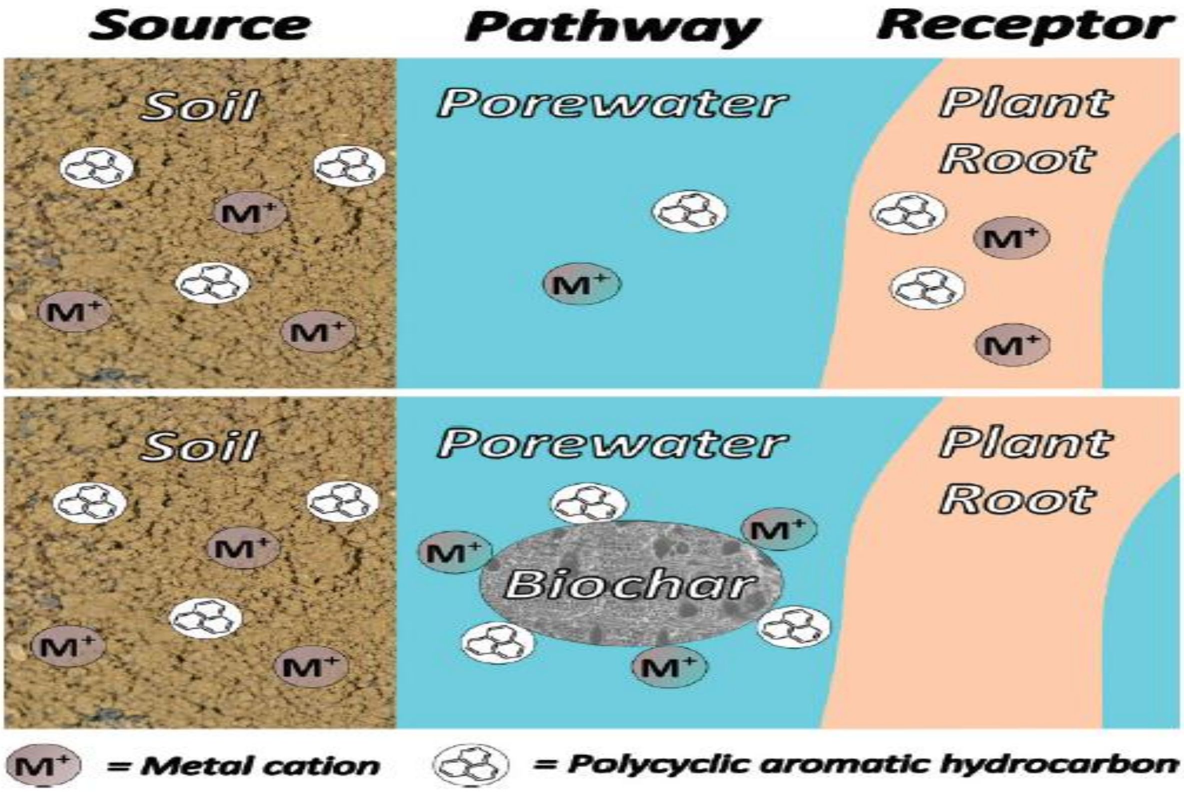


Figure 2.4: Diagram to demonstrate the remediation of organic and inorganic contaminants in soil by biochar, breaking a source pathway- receptor linkage [75].

A source is the physical location of a contaminant itself, or the location from which it is being emitted. A receptor is the location where it can cause harm (e.g., human tissue, other organisms, or water bodies). The pathway is the mechanism by which the contaminant moves from the source to the receptor. When a contaminant can move from a source to a receptor in sufficient doses to cause harm, then the contaminant is considered a pollutant and the soil is considered polluted soil. Biochar breaks source-pathway-linkages by adsorbing contaminants on its surface and thereby reducing the concentration of contaminants in the soil solution[76]. Remediation is thus achieved when biochar irreversibly adsorbs contaminants that come into the soil solution, eliminating the pathway to receptors (Fig 2.4). After sorption on the surface of the biochar, contaminants can be considered unavailable to organisms and no longer pose a risk of causing harm[75].

This adsorption occurs as biochar has a large surface area which enables it to adsorb heavy metals and organic pollutants. Consequently, it can potentially be used to reduce the bioavailability and leachability of heavy metals and organic pollutants in soils through adsorption and other physicochemical reactions[74]. This sorption occurs due to complexation of the heavy metals with different functional groups present in the biochar, due to the exchange of heavy metals with cations associated with biochar, such as Ca^{+2} and Mg^{+2}, K^{+}, Na^{+} and due to physical adsorption. Also oxygen functional groups are known to stabilize heavy metals in the biochar surface, particularly[77].

Alkalinity of biochar can also be partially responsible for the lower concentrations of available heavy metals found in biochar-amended soils. Higher pH values after biochar addition can result in heavy metal precipitation in soils[77]. As soil pH is closely related to the bioavailability of heavy metals in soils, it is suggested that biochar application can increase the soil pH and cation exchange capacity, and subsequently enhance the immobilization of heavy metals in soil[72]. In case of acidic contaminated soils, depending on the type of biochars and exchangeable cations (Na, Mg, K, and Ca) present in it, it could hold the key for the release of some of the these cations during sorption process with the heavy metal, and thus may enrich the stabilization process. Biochar can also stabilize heavy metals in the contaminated soils, improve the quality of the contaminated soil and has a significant reduction in crop uptake of heavy metals[78].

It has also been found that once sorption of the metal pollutant to the biochar had taken place it was not immediately reversible (reduced mobility). The fate of such contaminants, once sorption to biochar has taken place (reduced bioavailability), needs to be considered carefully, but again the microbial recalcitrant nature of biochar may be a beneficial trait[76]. Therefore, application of biochar can potentially provide a new solution for remediation of the soils contaminated by heavy metals. This effect of biochar on metal bioavailability varies with the types of biochar products as well as types of heavy metals. Therefore, when biochar is to be utilized as an amendment for the remediation of soils contaminated with heavy metals, one should take into account the types of heavy metals present in the contaminated soil, and the biochar production temperature as the biochar characteristics are dependent on pyrolysis conditions such as highest treatment temperature, moisture content of the feedstock, residence time, and the type of feedstock used[72].

Table 2.2: Effect of biochar application on the mobility of heavy metals in soil

Feed stock	**Production Temperature (°C)**	**Contaminant**	**Effect**	**Reference**
Sugar cane straw	400 - 700	Cd, Zn,Pb	Cd and Pb amount below detection limit in soil pore water while Zn concentration reduced up to 51% on different plants.	[3]
Chicken manure	500	Cu	CMB reduced Cu in the soil by 73 % and in the soil pore water by up to 10 times compared to control	[79]
Wood	550	As, Cd, Cu, Pb, and Zn	concentration of As, Cd, and Cu decreased in maize shoots, whereas the effects were inconsistent on Pb and Zn concentrations in the shoots.	[80]
Shrimp shells	Na	Pb,Cu	Mobilization of Pb(II) in soils have increased with increasing shrimp shells loadings while not Cu.	[81]
Bioenergy-waste	900	Cr	Bioaccumulation of Cr in plants grown in 5 % BC-amended TWS showed a decrease by 97 % compared to that of the BC-unamended soil.	[82]
Miscanthus straw	600	Ca,Pb,Zn	The reduction reached 71%, 87% and 92% for Cd, Zn and Pb	[83]

			respectively in the presence of 10% biochar.	
Rice hull	500	Cd, Cu, Pb, and Zn	From incubation studies, significant declines ([80 %) in the phytoavailable metal pool and that uptaken by lettuce.	[84]
Sugar cane straw	400-700	Cd, Zn	Biochar at 700 °C four times greater than 400 °C and up to seven-fold in the sorption of both Cd and Zn compared with the control	[85]
Chicken manure, green waste	550	Cd, Cu and Pb	Application of biochar significantly reduced NH_4NO_3 extractable Cd, Cu and Pb concentrations of soils and uptake by plants.	[86]
Bamboo	Na	Cd	Reduction of extractable Cd by 79.6 % within 12 days	[87]
Wood	200 and 400	Cd, Zn	Reduction in Zn and Cd leaching loss by >90 %	[88]
pine and oak wood and bark	400-450	As,Pb,Cd	oak bark biochar outperformed all others, removed ~70% of the As.	[89]

2.5.2. Environmental Benefits of Biochar

The overall effect of pyrolysis-biochar production on carbon abatement, prior to soils incorporation, can be described as the sum of two main factors: the carbon stored in char (related to CO_2 removed from the atmosphere) and the CO_2 emissions avoided through substitution of fossil fuels by combustion of pyrolysis products for energy[55].

Carbon sequestration using biochar

Carbon sequestration is the capture and subsequent storage of carbon to prevent it from being released to the atmosphere[64]. Producing biochar through pyrolysis of biomass and incorporating it into soil alters biogeochemical pathways to result in net C withdrawal from the atmosphere. Because biochar is resistant to microbial and physical decay, it can be used to sequester large amounts of C for over 1000 years[90]. Although afforestation still remains a feasible way of sequestering carbon by photosynthesis, the process is only carbon neutral. In contrast, the application of biochar to soils has the added advantage of turning carbon sequestration into a carbon negative system. This means that, because biochar is very slow to decompose, and yields a high carbon output over time, it is an effective, viable and sustainable C sequestration option[91].

This aspect of biochar that is critical to its inclusion in future policymaking is the ability to quantify biochar’s expected residence time in the soil. The degradation of biochar in soil is advantageous as about 50% of the carbon is removed in the pyrolysis process meaning that only about 50% of the carbon in the original biomass is actually applied to the soil meaning the carbon in the biochar is much more resistant to decay, the rate of loss levels off much faster and more carbon remains in the soil over the long-term[54]. A certain research undertook a global analysis of biochar sequestration potential and concluded that biofuel production using modern biomass could produce a biochar by-product through pyrolysis that results in 30.6 kg C being sequestered for every GJ of energy produced[74].

Greenhouse gas emission reduction

Literature gives evidence that the application of biochar for carbon sequestration in agricultural soils is a feasible option for achieving climate change mitigation. Since biochar has been proposed to draw CO_2 from the atmosphere, and because considering that methane (CH_4) and nitrous oxide (N_2O) greenhouse gas emissions are generally high, and pose a huge threat globally to agricultural management, the potential effect of biochar has also been proposed as significant in dealing with greenhouse gas emissions[92]. In addition, decomposition of biomass, including waste materials, can lead to the production of CH_4 and N_2O. Waste biomass is also the preferred feedstock for biochar production. The process of pyrolysis itself can also produce CH_4 and N_2O, although properly designed and managed pyrolysis systems can ensure these are captured for beneficial use, or suppressed to acceptably (according to relevant emissions standards) low levels[69]

2.6 Ash

Ash might be considered as the very first soil ameliorant used. Woodland burning was practiced as early as during interglacial times by primitive hunters and plant-gathering peoples to improve vegetation growth for their herds and wild animals. Often the purpose of ash application to soil is to improve the biomass production by providing plant nutrients (S, Ca, K, Mg) and reducing soil acidification. Ashes that have high alkalinity and acid neutralization capacity and are considered suitable for reclamation of mine spoils and revegetation of barren sites. Application of ash to sandy soils can improve soil texture and water-holding capacity and reduce the swelling potential of clays. In addition, ash can effectively immobilize trace elements in contaminated soils and reduce their toxicity.

According to previous research performed, the most common type of ash used is Fly ash from wood burning which is widely used for forest fertilization[26].Sugar cane bagasse ash (SCBA) has been used as a supplementary cementitious material (or simply referred to as pozzolan) for Portland cement in concrete[93]. Some of the researches show that the sugarcane straw ash contains high amount of silicon dioxide (SiO_2) which makes it a highly pozzolanic material[94].
According to all the researches done on biomass ash, the physical characterization is limited to the analysis of chemical composition and surface area measurement for the determination of its capacity to remediate soil. In order to demonstrate the potential ability of sugar cane straw ash in stabilization of soil tests were presented by preparing samples using different concentration of ash ***(***5%, 10% and 15%) at varying curing periods (3, 5 and 7 days)**.** The outcomes of these tests demonstrates that stabilization of soils using sugarcane straw ash improves the strength, facilitates to cope with environmental concerns through reduction of sugar industry waste material[94].

Even though the production of ash is environmentally unfriendly, ash is the major product of pre harvest fire in mechanical harvest of sugarcane straw. Consequently, the analysis of the possible capacity of ash for soil remediation has been considered to be one of the objectives of this study.

3. MATERIALS AND METHODS

3.1 Materials

The main raw materials for this research were Heavy metal contaminated soil and Sugar cane straw. One of the anthropogenic source of heavy metal contaminated wastewater, which eventually sinks in soil, is Metal electroplating and coating industries**.** One of the Industrial Units where such a process takes place is Small and Minute Enterprises found in Kirkos Sub city opposite to WabiShebele hosipital around Mexico. One of the projects this Enterprise is currently working is Metal plating which disposes liquid wastewater effluent loaded with heavy metals. This liquid waste was spiked on uncontaminated soil that is generally used to grow plants. Sugar cane straw was collected from a sugar cane stripping area in Yeka Sub-City around a place called karaon the road to Debre Birhan East of the country. This is the area where sugar cane would first be separated from the straw accompanying it before sale.

The equipments that were used to perform the experiment are listed as follows.

Table 3.1: List of Chemicals used

Chemicals	Usage
Characterization of Biochar and Soil	
Methylene Blue	Surface properties of biochar
$CaCl_2$	pH determination
N_2 gas	Pyrolysis process
Melich – II	CEC determination
HNO_3	Heavy metals Determination of biochar
EDTA	Heavy metals Determination of Soil
KBr Pellets	FTIR Spectra Determination

Table 3.2: List of Equipment and Materials and their use

Name of Equipment	Usage	Manufacturer (Model)
Equipment for the pretreatment and characterization of samples		
Oven	Drying Sugarcane straw	Memmert, Germany (100-800)
Sieve	Uniformity and Distribution of size	Retsch, Germany (AS200)
Mill	Size Reduction of Sugarcane Straw	Retsch,West Germany (SK1)
Atomic Emission Spectroscopy (AES)	Determination of Metallic Contents of soil samples	Spectro Analytical Instruments GMBH, Germany (ARCOS FHS12)
Production and Characterization of Biochar and Ash samples		
Furnace	Ash production	Nabertherm, Germany(SN 262014)
Spectro UV- Vis Split	Absorption capacity of biochar	Labomed.Inc, ,(UVD – 3200)
Elemental Analyzer	Determination of Elemental composition	Thermo Fisher Scientific(FlashEA1112 CHNS/O analyser)
Moisture Content Analyser	Moisture content determination	OHAUS, Switherland(MB45)
Fourier transform infrared (FT-IR)	Determination of functional group	PerkinElmer, USA, (Spectrum 65 FTIR)
Other Appliances		
Shaker	Mixing of samples	New Brunswick Scientific,USA(EXCELLA E24R)
Centrifuge	Separation of supertant from mixtures	CEPA,,(CS)
Analytical balance	Mass determination	Sartorius AG, Germany,(CP3245)
Crucibles	Proximate Analysis, Ash production	N/A
Desiccator	Regulating Temperature of materials	N/A
Filter papers	Filtering liquid samples	Qualitative filters, China(101)
PH Meter	Measurement of PH of samples	Voltcraft, Taiwan,(PH – 100ATC)
EC Meter	Measurement of EC of samples	VWR International,(D64295)

3.2 Methods

3.2.1 Preparation of raw materials

As stated earlier, the two basic raw materials for this research work were contaminated soil and sugar cane straw. As pre-treatment, the collected sugar cane straw was first cleansed with water for the purification of materials from any particles that would infect it. It was then dried in an oven with a constant temperature 105 degrees until it loses all the moisture and gives a constant mass. After the dry samples were ready, the size of sugarcane straw was first reduced manually using scissors to 2-3cm. The size reduction done using scissors was sufficient for the production of biochar as literatures show higher particle size of materials give better result in the charring process. Since ash production needs a smaller size distribution, a mill was used with a diameter of 2mm for reduction of size and then it was sieved with a diameter of 2mm.

It was not possible to obtain the soil which has been originally affected by the dumping of effluent from the plating process, thus, artificially contaminated soil was prepared by the method of spiking. Uncontaminated soil normally used for the purpose of growing flowers and plants was spiked. This uncontaminated soil sample was first spiked with 1Litre of wastewater from metal plating process**.** The heavy metal contaminated waste was sprayed onto the soil samples with continuous mixing to homogenize the distribution of the applied heavy metals.

After spiking, the soil was soaked in water and then mixed at regular intervals for four weeks which is followed by air drying. The wetting and air dry cycle process was continued for a month to allow sufficient mixing of the applied metals and soil to emulate field conditions. After preparation of artificially contaminated soil, the size of the air dried soil sample was reduced manually using a soft wooden material then it was sieved with 2mm mesh size to separate dissimilar size distribution. The size reduction of the soil was necessary to make the size equivalent with the biochar. Research shows the small and equivalent particle size of soil and biochar samples facilitates the remediation process. This equivalence provides a good environment for the better immobilization of metals. This shows the soil and biochar samples had the same size so the remediation process could be well facilitated.

3.2.2 Characterization of Raw materials

3.2.2.1 Characterization of Sugar cane straw

After the treatment stage is finished, the sample was characterized prior to going in combustion stages.

A. Bulk Density

Bulk density of the straw was determined by packing oven-dried sample of known mass into a graduated cylinder according to ASTM procedure (D 6683). The cylinder was then tapped until compaction was observed visually. The bulk density was then calculated by using the volume of the cylinder filled up by the sample in the following equation:

$$BulkDensity\ (kg/m^3) = massofsample\ (kg)/\ volumeofsample\ (m^3) \ldots\ldots\ldots\ldots\ldots \quad (3.1)$$

B. Proximate Analysis

As per ASTM standards, the proximate analysis of sugar cane sample was analyzed using the following methods.

1. Moisture content

The size reduced sugar cane straw sample was measured prior to being dried in an oven. Then each sample was left in the oven for a period of 24 hours while mass was measured each 6 hours until a constant mass is obtained. Then, the initial weight and the final weight will be used in the following formula to calculate the moisture content.

$$Moisture\ content = \frac{W_1 - W_2}{W_2} * 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3.2)$$

Where W_1 is original weight of the sample before drying, g

W_2 is weight of the sample after drying, g

2. Volatile Matter

The volatile organic compound was determined after burning the dry solids in a furnace at 950^0C for 7minutes. The sample was sent to a desiccator for about 20 minutes and weighed.

$$Volatile\ solids = \frac{W_1 - W_2}{W_1} * 100 \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (3.3)$$

Where W_1 is original weight of the sample before burning, g

W_2 is weight of the sample after burning, g

3. Ash Content

Ash content of the sample was determined by igniting the oven-dried sample from the moisture content determination in a furnace at 550°C for 2 hours. The sample was weighed and put in an open crucible. The substance remaining after ignition is the ash. The ash content is expressed as a percentage of the mass of the oven-dried sample.

$$Ash\ content = \frac{W_1 - W_c}{W_2 - W_c} * 100\% \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots . (3.4)$$

Where W_1 is the weight of ash, g

W_2 is original weight of oven dried specimen, g

W_c is the weight of crucible, g

4. Fixed Carbon

Fixed carbon is a calculated value. It is the difference between 100 and the sum of the percent moisture, ash, and volatile matter. All percentages shall be on the same moisture reference base. Thus, the fixed carbon was calculated as

FC = 100 – (%M+ %A+ %V) ……………………………… (3.5)

3.2.2.2 Characterization of Soil

The physical and chemical characteristics of the soil were determined in Environmental and Organic Laboratory of AAiT Chemical and Biochemical Engineering Department. pH was measured in distilled water and in 0.01M $CaCl_2$ in a 1:5 soil to solution ratio. Electrical conductivity (EC) was measured in distilled water at a soil to water ratio of 1:5.

The basic technique this research used for the determination of effectiveness of BC and ash samples in remediation is comparison of quality of raw and remediated soil. To do this, the original amount of contaminants in raw soil in addition to the micro and macro nutrients of soil which eventually help in the determination of CEC of soil were determined. The procedure for each analysis is found in detail in section 3.2.6.1 and 3.2.4.4 respectively.

3.2.3 Production of Biochar and Ash

Biochar and Ash were produced in the Research Labratory of AAiT Chemical and Bio Engineering Department. A Pyrolyser setup having a tubular reactor of stainless steel 1m length inserted in a tubular furnace with a capacity to be heated with a maximum temperature of 700°C. The reactor was then flashed with N_2 gas so as to make the environment inside inert.

After the preparation of Sugar cane straw samples ready for the carbonization stage, a sample of 80g sugar cane straw was put in a pyrolyser. All runs were conducted in batch process. Three runs were performed by keeping the heating rate constant at 10°C per minute i.e applying slow pyrolysis until it reaches a final temperature of 300, 400 and 500°C. these temperature ranges were selected as biochar used for the purpose of improving agronomic soil properties are produced at a temperature range of 300°C to 700°C[85]. All the carbonization process took a period of one hour and were conducted in batch process. After the process was finished, the biochar was allowed to cool down at room temperature and stored prior to characterization.

Sugar cane derived ash on the other hand was produced in a muffle furnace using small ceramic crucibles with a temperature of 700°C until it reaches a point where all the raw sugar cane straw has been fully converted to ash. This process took two hours to complete. The ash produced was once again allowed to cool down to room temperature and stored until it was mixed with soil.

3.2.4 Characterization of Biochar

Biochar was characterized for its physical and chemical properties using various technologies. The equipment to be used for characterization and their respective purpose is listed in the materials section.

3.2.4.1 Proximate Analysis

Proximate analysis of the biochar produced from sugar cane straw was determined using the same procedures used for determination of sugar cane straw (section 3.2.2.1). Three runs were performed to produce biochar at a temperature of 300°C, 400°C and 500°C. These products obtained were assessed for their moisture value content, volatile matter, ash content and fixed carbon. The values were compared to determine the effect of temperature on the properties of biochar produced form the same raw material.

3.2.4.2 Yield

The Percentage yield of biochar from each experiment run was calculated using the following equation:

$$\%\,\text{Yield of biochar} = \frac{\text{Wt. of biochar produced}}{\text{Wt. of pyrolysis feedstock}} \times 100\% \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(3.6)$$

3.2.4.3. Methylene Blue Absorbance Analysis

The methylene blue absorption shows the maximum amount of dye adsorbed on 1.0 g of adsorbent. In this case, a stock solution of 1000ppm was prepared with 1g of methylene blue and 1000ml of water. Then the absorption capacity was measured by placing 10.0 mg of biochar in contact with 100.0 mL of a methylene blue solution at a concentration of 150ppm for biochar samples prepared from three runs for 24 h at room temperature. Then samples were shaken at 150 rpm for 24 hrs. After equilibrium was attained, the sample was centrifuged at 5000 rpm for 30minutes and then the supernatant was separated. The remaining concentration of methylene blue was analyzed using a UV/Vis spectrophotometer at 645 nm. The percentage of MB adsorbed in to Biochar can be calculated as

$$Percentage\ of\ MB\ removal = \frac{C_1 - C_0}{C_1} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.7)$$

The amount of methylene blue adsorbed from each solution is calculated by the Equation :

$$q_e = \frac{C_o - C_e \, . \, V}{M} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots .. (3.8)$$

where Co(mg L^{-1}) is the concentration of the methylene blue solution at starting time (t = 0), Ce (mg L^{-1}) is the concentration of the methylene blue solution at equilibrium time, V (L) is the volume of the solution treated and M (g) is the mass of the adsorbent.

3.2.4.4 Cation Exchange Capacity and Exchangeable Nutrients

Cation exchange capacity (CEC) was quantified by Mehlich-3 which is a multi-element soil extraction estimates plant availability of most macronutrients and micronutrients on soils from acid to neutral pH using a dilute Acid-Fluoride-EDTA solution of pH 2.5. For the analysis, 2.0 ± 0.05 g of air-dried BC was passed through a 10 mesh sieve and added to 20.0 ml of Mehlich-3 extraction solution in a bottle. The extraction was shaken (200 rpm) for 5 minutes and filtered suspension through a Whatman filter paper. The Exchangeable bases of the extractant was analyzed using ICP-AES. This result was used for the determination of CEC according to Rhodes,1982. This analysis was performed in the Laboratory of Horticoop Ethiopia PLC located in Debrezeit.

3.2.4.5 Heavy Metal Content Analysis

Prior to being used for remediation, The heavy metal content of biochar samples were analyzed to get information about the possible existence of heavy metals in biochar to be used for remediation. This was done using Concentrated HNO_3 for the extraction of heavy metals specifically Cr and Ni. The procedure followed is the same as described above for the determination of Micro and macronutrients, with the only difference being the extracting solution. This analysis was performed in the Laboratory of Horticoop Ethiopia PLC located in Debrezeit.

3.2.4.6 FTIR Analysis

The changes in functional groups can be observed when biochar is subjected to Fourier transform infrared spectroscopy (FTIS/FTIR).The functional groups attached to the molecule, produce characteristic and reproducible absorptions in this spectrum. This information determine if there is unsaturation and/or aromatic rings in the structure. Then, it is possible to deduce whether specific functional groups are present. These changes of samples was measured on Spectrum 65 FTIR in the range 4000-400 cm^{-1} using KBr pellets.

3.2.4.7 Elemental Analysis

The amount of carbon, hydrogen, nitrogen and oxygen in percentage in biochar was determined using an Elemental Analyser in the laboratory of Chemistry department of Addis Ababa University. CHNS composition of sample was determined by using the grinded and dried sample combusted in a furnace with temperature of 900°C. Out of the three biochars produced from three runs, only 500°C Biochar was taken to be the optimum based on preceding research.

3.2.4.8 pH and EC

All meters were first calibrated routinely at two point with buffer solutions of pH of 4 and 7**.** Then, The pH and EC of biochar samples was measured in the biochar/water slurry with 1:10 biochar/water ratio using after shaking with deionized water for 24 hours.

3.2.5 Mixing of contaminated soil with biochar and Ash

Contaminated soil was mixed with varying amount of biochar and ash. They were mixed in a set of pots while maintaining their water requirement. The remediation capacity of biochar produced at varying temperature and ash were tested by considering the effect of these factors.

Table 3.3: Experimental factors and corresponding levels Biochar

	Type of Remediation Material			
	Biochar			**Ash**
Factors	**Levels**			
Carbonization Temperature (°C)	300	400	500	700
Amount of Remediating material(%w/w)	4	7	10	10
Time of incubation (days)	150	180	210	210

The remediation materials and the soil were thoroughly mixed to obtain homogeneity. A control treatment following the same procedure was also prepared, but without adding any amendment. Pots were then irrigated various times a week with the same amount of water for each pot. The mixture was incubated for a period of days listed about in the table. The heavy metal content of soil was analyzed at the end of each incubation period to determine the effect of time to the capacity of heavy metal immobilization of biochar and ash. Thus, the factors that were varied for the remediation stage were soil to remediating material proportion and incubation period. The ranges of dosage and time were suggested from previous works perfomed on assessing biochar capcity using pot experiments [3, 79, 85]. These researches are listed in table 2.2 of literature review.

3.2.6 Analysis of Remediated soil

3.2.6.1 Heavy Metal Content Analysis

A metal immobilization assay was carried out, according to the procedures followed in section 3.2.4.5 to get information about the ability of biochar and ash to immobilize heavy metals in the incubated soil. After the incubation period, Heavy metals were extracted from soil sample by shaking it with DTPA solution for 2h. This was followed by the determination of Heavy metals using ICP-AES. Then, the immobilization capacity can be calculated according to Park et al (2011) as follows.

$$\text{Immobilized metal (\%)} = \frac{\text{Metal content in control} - \text{Metal content in treated sample}}{\text{Metal content in control}} \times 100 \quad \text{.. (3.9)}$$

3.2.6.2 pH

All meters were calibrated routinely at two point with buffer solutions of pH of 4 and 7 before measuring the pH of a soil sample. The same procedure for the measurement of pH of raw soil was used (Section 3.2.2.2).

3.2.6.3 Cation Exchange Capacity and Exchangeable Bases

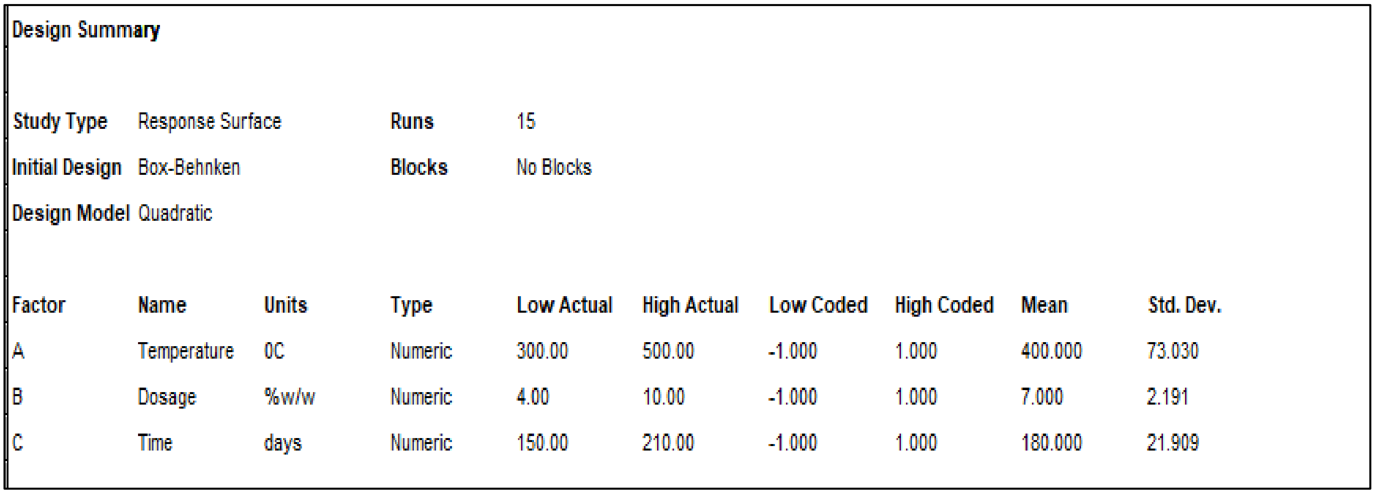
As one of the consequences of soil contamination is retarding its capacity for retention and exchange of useful nutrients, the CEC of an optimum remediated soil was measured to verify the effect of biochar on soil. The same procedures were followed as for biochar(Section3.2.4.4.).

3.3 Experimental Design and Statistical analysis

The set of experiments that were performed were based on factorial design having three factors that were varied for a set of three levels. The carbonization temperature, dosage and incubation for BC was varied within three levels while ash production is just limited to one level for each factor. This gives a total of 27 experiments for BC and 1 experiment for ash giving a total of 28 experiments. They were analyzed to conclude which is to be accepted as the best situation for the research. In order to evaluate the effect of these main factors (BC production temperature, BC dosage and Incubation time) independently and their interactions effect, the data were analyzed using Design Expert Software Version 7.0.0 for Analysis of variance (ANOVA) table, normal % probability versus residuals graph, and predicted versus actual values graph were used to diagnose the experimental data.

Box–Behnken statistical experiment design consisting of a three-factor and three-level pattern giving a chosen fifteen experiments with one center point analysed three times for assuring duplicity of results. This design was composed of a 12 factorial design (runs 1–12), 3 center points (runs 13–15) thus 15 experiments were needed in total. The responses considered were the concentration of heavy metals Cr and Ni in soil. The significant terms in the models were identified by analysis of variance (ANOVA) used for comparison of means of each response. Significance was judged by determining the probability level that the F-statistic calculated from the data was less than 5% and accepted at 0.05 level of probability ($p<0.05$).

Table 3.4: Summary of Experimental Design (Output from Design expert)



Design Summary

Study Type	Response Surface	**Runs**	15
Initial Design	Box-Behnken	**Blocks**	No Blocks
Design Model	Quadratic		

Factor	Name	Units	Type	Low Actual	High Actual	Low Coded	High Coded	Mean	Std. Dev.
A	Temperature	0C	Numeric	300.00	500.00	-1.000	1.000	400.000	73.030
B	Dosage	%w/w	Numeric	4.00	10.00	-1.000	1.000	7.000	2.191
C	Time	days	Numeric	150.00	210.00	-1.000	1.000	180.000	21.909

3.4 Limitation of the Study

The pyrolyser employed for the production of biochar was not functioning well affecting the production of BC with possibly having lesser quality and capacity than expected. Although it was attempted to examine all available samples for the analysis of heavy metal contamination in soil, this was not possible as it required much budget leading to characterization of fewer samples than planned. In addition, metal lubricating factories were not willing to give the contaminated soil for the analysis. Only one factory was willing to give their liquid waste which was used for the preparation of artificially contaminated soil.

4. RESULTS AND DISCUSSION

4.1 Characterization of sugar cane straw

The proximate analysis and bulk density of raw sugar cane straw was performed before combustion. This analysis included ash content, moisture content, volatile matter and fixed carbon. The results of the analysis are shown below in Table 4.1. The detailed calculation is included in Appendix A.

Table 4.1: Characteristics of sugar cane straw

Determination	Results
Proximate Analysis	
Moisture Content	7.1%
Ash Content	1.74%
Volatile Matter	85.4%
Fixed Carbon	5.37%
Physical Property	
Bulk Density	0.3g/cm^3

The results obtained above were compared with results gained from previous research performed on the same raw material and other biomasses [67,96,114]. These results were analyzed to determine whether this raw material has the capacity required to fulfill the final goals of this research.

The moisture content (7.1%) is relatively low and in agreement with what is required of biomass. The moisture content in the raw biomass would affect the energy consumption and decrease the efficiency of the conversion process and also increase the cost of transport[95]. The low ash content of straw (1.74%) is useful as it shows the suitability of the raw material in thermo chemical conversion as it affirms the abundance of organic matter. The high volatile matter (85.4%) shows in combustion, this raw material is prone to releasing volatile gases in the environment. This negative impact can be avoided using a chiller with a glass condenser for trapping the gases before they escape to the environment and also it has been tried to direct the VOCs into a water bath. The aim of directing the gases into a water bath is to trap the harmful gases (especially CO and CO_2) from escaping to the atmosphere and also to convert the CO_2 gas into carbonic acid, which is a harmless substance[96].The bulk density of this biomass ($0.3 g/cm^3$) is relatively small. For this reason it is generally economically feasible to transport unprocessed biomass. In addition, the fact that fixed carbon result (5.37%) is low has a good effect on the specific use this biomass is adopted for in this research.

4.2 Characterization of Biochar

The chemical and physical properties of biochar produced by varying temperature from 300°C to 500°C were analyzed. These properties are useful for determining the absorption capacity of biochar produced from this specific biomass used in this study. Moreover, these properties assist in the examination of the effect of temperature for the production of an optimal biochar possessing the qualities necessary for enhanced metal uptake.

4.2.1 Proximate Analysis

The proximate analysis including ash content, moisture content, volatile matter and fixed carbon of three biochar samples produced at varying temperatures were calculated and the result is presented in Table 4.2. The detailed calculation is presented in Appendix A.

Table 4.2: Characteristics of Biochar

Determination	Results		
	300°C BC	400°C BC	500°C BC
Proximate Analysis			
Moisture Content	7.17%	10.23%	7.5%
Ash Content	35.2%	39%	42.8%
Volatile Matter	49.4%	32%	20%
Fixed Carbon	8.63%	18.77%	29.7%
Physical Property			
Bulk Density	$0.25 g/cm^3$		
Elemental Analysis (dry basis)			

C (%)	61.18
H (%)	2.77
N (%)	-
S (%)	-
C/H	0.54

The table presented above shows the fixed carbon and ash content of biochar increased with increasing severity of temperature while volatile matter seems to decrease. This seems to be as a result of that pyrolysis process releases volatile matter during the charring procedure. In addition, the removal of volatile carbon rather than fixed carbon has attributed for the increase of fixed carbon with the increase of temperature. This also indicates while the magnitude of heat increases, the mass of overall biomass is reduced leading to increase of fixed carbon content. This might due to the fact that the increasing temperature resulted in the further crack of the volatiles fractions into low molecular weight liquids and gases instead of biochar[46]. Meanwhile, the dehydration of hydroxyl groups and thermal degradation of cellulose and lignin might also occurred with the increasing temperature [97].

The increase in ash content from 300–500°C is the result of a progressive concentration of minerals and destructive volatilization of ligno-cellulosic matters as temperature increased[98]. This is expected as ash remains in the solid fraction whereas the organic matter undergoes thermal decomposition, resulting in weight loss in the C-containing fraction[46]. The moisture content result seems to fluctuate around close digits which shows the charring process didn’t have much effect on decreasing the moisture content of biomass before and after pyrolysis.

Moreover, sugar cane straw biochar shows similar bulk density compared to the particles of raw biomass. The ultimate analysis shows that biochar is moderately carbonaceous, with a carbon content of 61.18%. The high carbon content of biochar is advantageous in terms of maximizing the amount of carbon storage and could be used as an energy resource or for soil adsorption of pollutants [99]. The mid range value of H/C ratio (degree of aromacity) also indicated a great amount of original organic residues. As H is primarily associated with organic matter, the H/C atomic ratios could be described as an indicator of carbonization[100].This result is likely to be an indicative measure of the overall biochar stability in the soil[46]. Also, as with most biochars from biomass, the percentage of nitrogen is negligible. The absence of S and N indicated that using sugar cane straw in a thermochemical conversion process have inconsequential production of NOx and SOx to pose any threat of pollution to the environment.

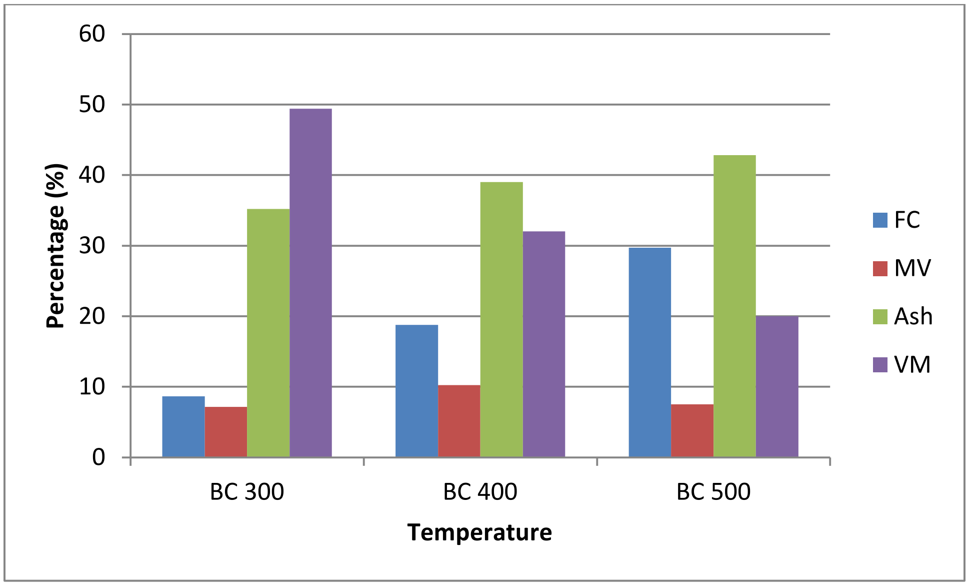


Figure 4.1: Proximate analysis of biochar

In general, all results are in agreement with previous studies done on similar and other biomasses showing acceptable results can be expected from biochar produced.

4.2.2 Biochar Yield

Carbonization Results

During the pyrolysis process for the production of biochar and ash, the only factor that was varied was temperature. Biochar was produced within three run by varying the temperature from 300 -500 degrees with a residence time of 1hr and heat flow rate of 10°C/min while ash was produced at a temperature of 700 degrees in a muffle furnace. 80g of size reduced sugar cane straw was used for each run of biochar production while 5g were used for the production of ash.

Table 4.3: Amount of Biochar and Ash production

Biochar Produced		
Run	Carbonization Temperature(°C)	Amount Produced(g)
1	300	40g
2	400	22g
3	500	19g
Ash Produced		
1	700	1.58g

From the results above, it can be observed highest amount of biochar was produced at the lowest pyrolysis temperature of 300 degrees. This amount decreases at the severity of temperature increases. From these results, the Biochar and Ash yield can be calculated as follows.

Table 4.4: Biochar and Ash Yield

Biochar Yield		
Run	Carbonization Temperature(°C)	Yield(%)
1	300	50
2	400	32
3	500	23.7
Ash Yield		
1	700	31.6

The effects of pyrolysis temperature on biochar yield are illustrated in the Figure 3.2 below. The char yields are negatively correlated with increasing pyrolysis severity (i.e. increased temperature). The results above are coherent to the ones predicted in literature.

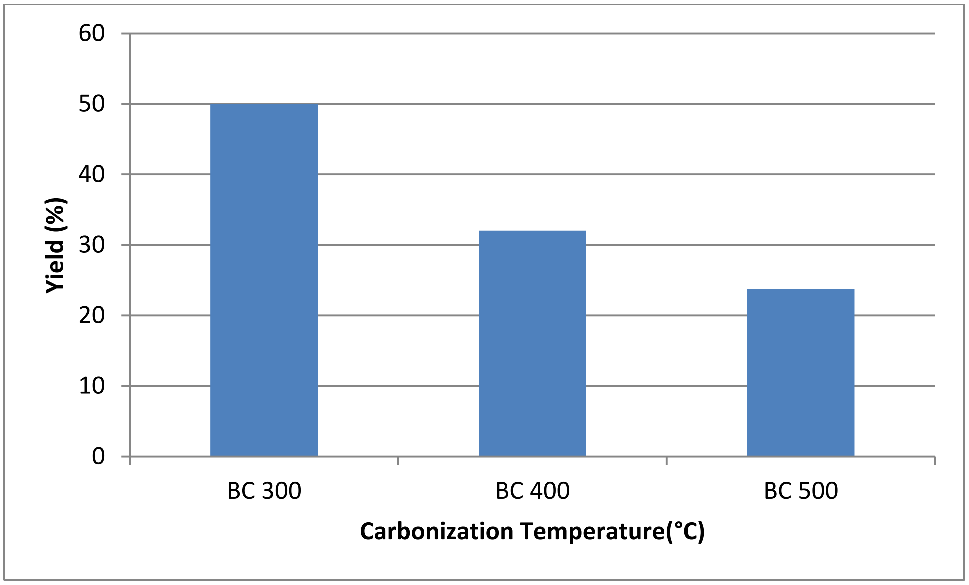


Figure 4.2: Biochar Yield at various temperature

The degree of carbonization for biochar was accelerated with increasing pyrolysis temperature from 300°C, 400°C to 500°C. The primary thermal degradation of biomass happens during pyrolysis. The pyrolytic volatiles are further broken into low molecular weight organics and gases as the pyrolysis temperature increases[101].Also this result was probably due to most of the lignocellulosic material was decomposed at this increase of temperature range [102].

4.2.3 Methylene Blue Absorption

Methylene blue is commonly the preferred model compound for adsorption purposes in the scientific world to determine quality of the adsorbent. From the information obtained from the absorbance of biochar produced at three runs, the absorbance capacity of biochar and the percentage removed of Methylene Blue at the application of each adsorbent has been calculated as follows.

Table 4.5: Adsorption Data of Methylene Blue

Biochar	Absorbance	MB Conc (mg/L)	q(mg/g)	% Removal
BC300	2.225	114.78	17.61	23.48
BC400	2.192	112.76	18.62	24.8
BC500	2.139	109.5	20.25	27

The adsorption characteristic of a biochar is determined by its porous structure and surface chemistry[35]. As temperature increases, it can be seen the surface properties are magnified giving biochar better porous structure. This allows biochar to immobilize particles better. Thus, the biochar produced at 500°C shows better the surface area and pore volume showing activating the raw material at 500°C results better adsorbent. This is because The VOCs are released out and the carbon structure is firm, so that high adsorption can take place[103]. As temperatures increases, more volatile gasses are released from the biomass, the vesicles on the surface of BC busted after cooling, thus it exhibits a number of pore structure[104]. The low percentage removal percentage of the biochar was attributed to the malfunctioning of pyrolysis setup which has been one of the impeding factors during this study.

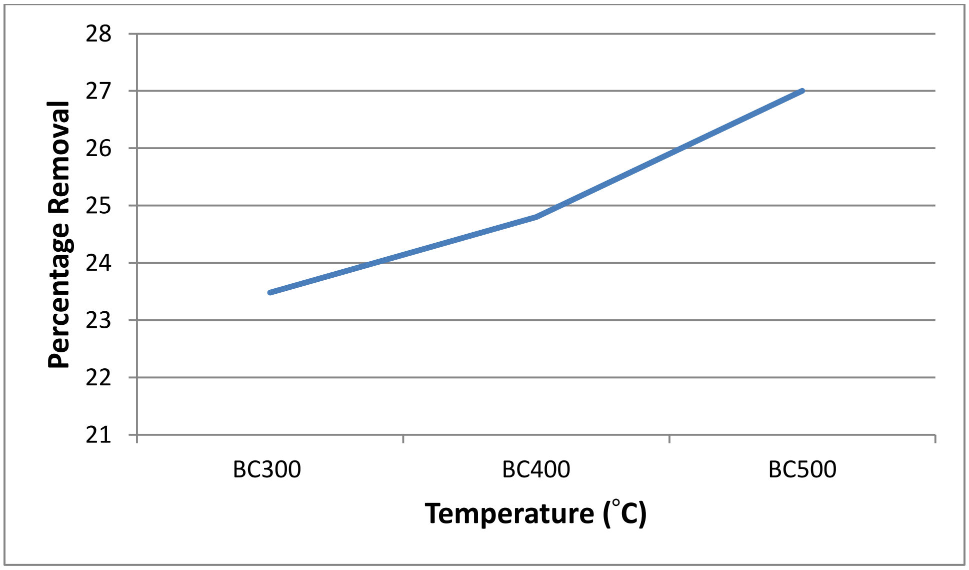


Figure 4.3: Methylene Blue absorbance of BC

The significance of pyrolytic temperature leads to the suggestion that BC produced at low pyrolytic temperature may be appropriate for regulating release of fertilizer nutrients [105], while high temperatures would lead to a material analogous to AC in environmental remediation [106].

4.2.4 pH and EC

Table 4.6: pH and EC results of Biochar

Biochar Type	pH Results	Electron Conductivity(dSm−1)
BC 300	7.97	0.708
BC 400	8.38	0.158
BC 500	9.24	0.437

Recent studies show that most biochars from pyrolysis processes are usually alkaline in nature ranging from pH 7.5-9.4. The pH of biochar is related to feedstock nature and applied temperature in the production process. Lower temperature and hold time resulted in low pH but still alkaline in nature. The significant pH change between biochars, which were produced at low and high temperatures, can be explained with the change of chemical structures during pyrolysis process[35]. The pH of the biochar, next to its ash content, is likely to be correlated with the presence of oxygen functionalities in the biochar: during thermochemical conversion with lower process intensity, more labile and more oxygenated carbon is retained. Consequently, at higher pyrolysis severity, the amount of carboxyl groups in the resulting biochar has been reduced and/or the acidic groups have become deprotonated to the conjugate bases resulting in more alkaline pH of the biochar in suspension[46]. These pH values of Biochar make them useful in specifically acidic soil which affect plant growth highly. The alkaline nature biochars would be useful to increase the pH of acidic soils at risk of aluminum toxicity. It is reported that the presence of carbonates and anions in biochar leads to a decrease in soil acidity by reacting with soil H+[107].

The EC value of biochar seems to fluctuate. According to previous studied, many variables are affecting the electrical conductivity of carbonaceous powders including the shape of grains, size of grains, and the amount of compression in the test cell[108]. Thus, the measurements reported in the literature in many cases are very specific to the conditions used and they can be best used for comparisons within the samples reported in the same study. It can be concluded the EC value of biochar increases with increase of severity of pyrolysis conditions. This can be attributed to the generation of more graphite-like structure along with lower content of heteroatoms resulting in fewer barriers for electrons to be transferred within microcrystalline units[109].In previous literatures, results regarding the effect of EC of biochar on soil is quite limited. Generally, EC values of biochars used for soil amendment are between 0.4 to 3.2 dS/m, depending on this range, all biochars have the capability to be a good soil amendment and reduce the EC of saline soil. Hence, in general, BC with higher EC values has a lower capacity to remediate soil with high salinity as it has less capacity to provide it with better water holding capacity, reducing ion toxicity**.**

4.2.5 FTIR spectroscopy

In lignocellulosic feedstocks, the surface functional groups present are mostly hydroxyls (-OH), carboxylic acids (COOH) and small alkyl chains such as methyl groups (-CH3). With this kind of surface chemistry, feedstocks tend to be polar, hydrophilic and relatively reactive[54].

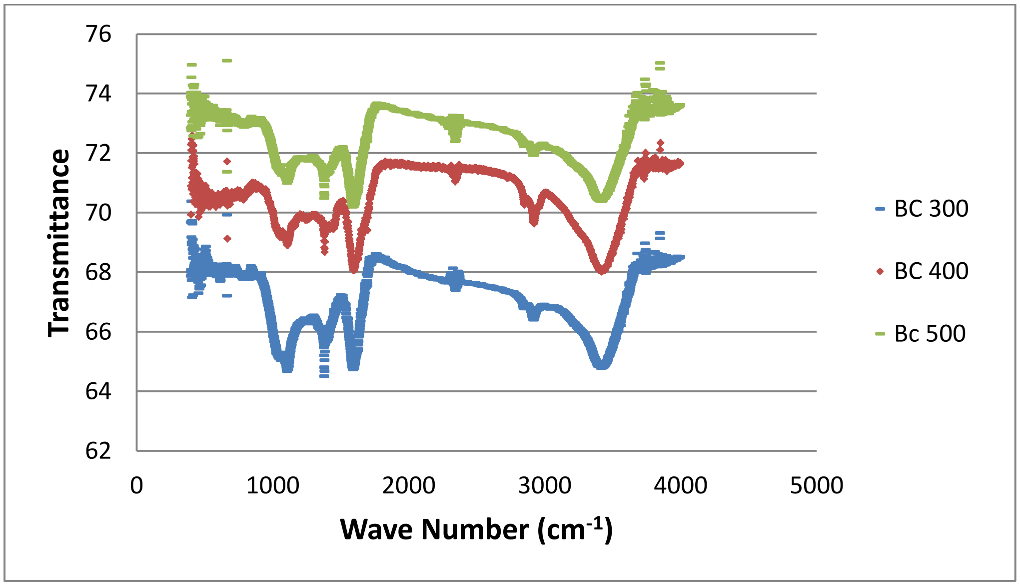


Figure 4.4: FTIR spectroscopy analysis of Biochar

As it can be observed on the figure 4.4, The feedstock spectrum of sugarcane straw biochar is dominated by the O-H stretch, aliphatic C-H stretch and carboxyl C=O stretch and aromatic C= C stretches. The C-H stretch vibrations for methyl and methylene are the most characteristic in terms of recognizing the compound as an organic compound containing at least one aliphatic fragment or center. Any band structures observed between 3150 and 3000 cm-^{1} are almost exclusively indicative of unsaturation and aromatic rings[110]. From the figure it can be observed, As the pyrolysis temperature increased, FTIR spectra of biochars revealed a decrease in the stretching of O–H (3200–3500 cm-^{1}) and C–H (2935 cm-^{1}), this was attributed to the acceleration of dehydration reaction in biomass[111], which suggested a decrease in the polar

functional groups with an increase in pyrolysis temperature. This is in agreement with previous studies that have shown that the biochars produced at temperatures of 300–400°C exhibit broad alkyl signals and carbohydrate bands; these bands were not detected above 400°C[112].
The peaks between 1688 and 1702 cm-^{1} correspond to C=O stretching, which is an indication of carboxylic and lactonic groups Aromatic C=C ring stretching were observed between 1414 and 1598 cm[113]. In particular, biochars began to increase aromatic C=C stretching (1440 cm-^{1}) with increasing pyrolysis temperature. As the pyrolysis reaction progresses, oxygen and hydrogen are removed, leaving the remaining carbons to form new aromatic carbon-carbon bonds. The “orderliness” of the aromatic structures also increases with increasing temperature, forming gradually larger sheets of interconnected aromatic rings[54].This result is likely due to the degradation and depolymerization of cellulose, hemicelluloses and lignin[105].

The peaks between 873 and 798 cm-^{1}correspond to changes in aromatic structures such as aromatic hydrogen[35]. While the peaks between 1050 to 1150 correspond to aromatic CO stretching of structures of alcohols. They exist as three distinct classes – primary, secondary and tertiary – distinguished by the degree of carbon substitution on the central hydroxy-substituted carbon[110].It is worth noting that there is not much need to produce biochar at very high temperature (700–800°C) in order to preserve stability character, since these temperatures may reduce the amount of functional groups in the structure, limiting the chemical properties of the biochar as soil amendment. Thus, a lower temperature may be suitable for the application of the biochars for the improvement of soil fertility. In contrast, higher-temperature pyrolysis selects functional groups and produces a predominantly aromatic presence in chemical composition, consequently resulting in the formation of recalcitrant structure[112].

4.2.6 Cation Exchange Capacity (CEC)

Cation Exchange Capacity is an important indicator for potential application of biochar into soil and carbon sequestration. The presence of charged, hard Lewis ligand functional groups on the biochar surface gives biochar its ability to attract, retain and exchange basic cations (readily available for plants to absorb), which can be used to enhance nutrient holding capacity of the soil, minimizing nutrient losses by leaching[35]. According to the analysis performed, the CEC was found to be 29.9 calculated according to the formula presented in the methods section. This result is considered to be in a high range thus, we can expect that the soil application of the biochar from sugar cane straw would lead to the great improvement in soil fertility.

4.2.7 Heavy Metal Content Analysis

The heavy metal content analysis of biochar prior to usage is an important factor as Heavy metals present in the feedstock are most likely to remain and concentrate in the biochar[51].

Table 4.7: AAS analysis of biochar

Sample No.	Cr conc (ppm)	Ni conc (ppm)
1	0.00278	0.00494
2	0.00547	0.01032
3	0.00846	0.01656
4	0.01101	0.02245

The heavy metal analysis of biochar shows that the concentration of Cr and Ni found in biochar is below 0.01 and 0.03 for Cr and Ni respectively. According to the result of the analysis, these results are below detection limit. Thus, biochar poses no risk to the increase of the concentration of soil. Moreover, it can be concluded the concentration of heavy metals that will eventually be immobilized to biochar are directly obtained from contaminated soil.

4.3 Characterization of Soil

Three biochars produced at the variation of temperature were mixed with contaminated soil. The dosage of biochar was varied from 4%w/w to 10%w/w of soil. The properties that indicate the remediation of soil were determined at a time interval of 150 days, 180days and 210days. These factors show interactive effect of biochar produced at varying temperature, dosage amount and incubation period on the remediation of heavy metal contaminated soil.

At the same time, Ash was produced at a particular temperature of 700 degrees. It was then mixed with contaminated soil at dosage of 10%w/w. The properties of this mixture were measured at the final time period of 210days. The ability of ash to remediate soil was characterized analyzing only the remediated soil. There was no previous research performed extensively on ash for soil remediation from heavy metals, thus no methods of characterizing it. Moreover, this research is mainly concerned with examining whether ash has this capacity.

4.3.1 pH and EC of Soil and Soil- Biochar Mixtures

The pH value of soil and Soil – Biochar mixtures was measured in water and $CaCl_2$ solution. The results of these two methods was quite close, thus, the result of that measured with water has been presented to avoid repetition.

Table 4.8: pH values of soil – biochar mixtures

BC type	**Incubation Time**								
	150 days			180 days			210 days		
	Dosage Amount of Biochar (%w/w)								
	4	7	10	4	7	10	4	7	10
BC 300	5.62	6.0	5.75	6.12	6.38	6.39	6.41	6.57	6.68
BC 400	5.8	5.83	6.0	6.18	6.19	6.38	6.46	6.56	6.77
BC 500	5.8	6.0	5.94	6.39	6.38	6.5	6.38	6.41	6.58

The pH value of control soil with 0%w/w had a closely neutral value of 4.8 which is highly acidic. In reference to previous work done, the pH value of soil exposed to heavy metals ranges from 5.5 - 6.5, which shows more of an acidic property. Different species of plants have different optimum conditions. Most plants perform best in a soil that is slightly acidic to neutral (pH 6 to 7)[35]. Biochar releases cations into the soil after addition, which can slightly raise the pH and EC. This can facilitate HMs bioavailability to the plants and can be translocated into the shoot, especially in acidic soil[114]. From the table above, it is evident biochar increased the pH value of soil significantly with the increase of incubation time and dosage. That is from an acidic value of 4.8 of raw soil to a maximum nearly neutral value of 6.77 was obtained at BC 400 with the highest dosage and incubation time.

The pH value of ash remediated soil was found to be 7.5 which is the highest value obtained compared to the pH values of biochar remediated soil. This shows ash has a greater capacity to remediate highly acidic soil even more so than biochar.

The Electron Conductivity result of soil showed to be 0.46 (dSm^{-1}). EC is an important indicator of soil health. It affects crop yields, crop suitability, plant nutrient availability, and activity of soil microorganisms which influence key soil processes. According to literature, Soils with EC values above 4 dS/m are considered to be saline soil[35]. Thus, The EC value doesn't show high salinity of soil. In most of the cases, high salinity of the soil adversely affects the rate of plant growth and harvest yield by causing ion toxicity and reducing water uptake by plants. This shows contaminated soil used in this study doesn't have salinity results that are regarded as unfavorable.

4.3.2 Exchangable Bases and Cation Exchange Capacity(CEC)

The presence of phytotoxic concentrations of contaminants in soil results in an imbalanced ratios of key nutrients, poor physical condition of soils and low cation exchange capacity. These factors limit the establishment of vegetation preventing or restricting the ability of soil to perform its normal functions. The ability of biochar to increase nutrient retention in soils is due to the increases in cation exchange capacity (CEC) that result because of application[51]. In addition, Biochar has an impact on addition and nutrient retention. The ash in biochar contains plant nutrients, mostly bases such as Ca, Mg, and but also Phosphorous and micronutrients including zinc (Zn) and manganese (Mn)[69].

Table 4.9: Exchangable Bases and Cation Exchange Capacity(CEC)

Soil Characteristics	Before Remediation(mg/kg)	After Remediation
P	47.17	64.33
K	1034.79	2521.96
Ca	2468.55	2426.05
Mg	793.44	762.81
S	193.98	693.81
CEC	20.68 Meq/100g Soil	29.20/100g Soil

From the results, it can be observed, the concentration of plant nutrients specifically Phosporous, Calcium, Sulfur and Potassium has increased while magnesium has shown a small decrease. The concentration of P, K is almost twice that of the control. Thus the application of BC addition led to an increase in the concentration of macronutrients (P, K, Ca, and Mg) in soil and consequently in soil CEC. This increase was due to the high concentrations of available P and exchangeable K found in the biochar[65].

4.3.3 Heavy metal content analysis

This analysis is the major indicator of the capacity of sugarcane straw derived biochar and ash for the immobilization and subsequent decrease in bioavailability of heavy metals in soil and plants respectively. With the help of statistical design, the independent and interaction effect of temperature in production of biochar, dosage amount of biochar to soil and incubation were determined. These results show which of these factors give the strongest effect on the immobilization process. The results of the analysis is given below.

Table 4.10: Concentration of Cr and Ni in biochar remediated soil

Run	Temperature (°C)	Dosage (w/w%)	Time (days)	Cr		Ni	
				Conc (ppm)	Percentage Immobilized (%)	Conc (ppm)	Percentage Immobilized (%)
1	300	4	180	1700	61.7	1200	63.2
2	500	4	180	1378	69.0	702	78.4
3	300	10	180	1620	63.5	1158	64.5
4	500	10	180	1201	72.9	632	80.6
5	300	7	150	1731	61.0	1289	60.5
6	500	7	150	1358	69.4	732	77.5
7	300	7	210	1511	66.0	1012	68.9
8	500	7	210	1081	75.6	601	81.5
9	400	4	150	1667	62.5	1001	69.3
10	400	10	150	1511	66.0	988	69.7
11	400	4	210	1431	67.8	782	76.0
12	400	10	210	1323	70.2	698	78.6
13	400	7	180	1543	65.2	1000	69.3
14	400	7	180	1554	65.0	837	74.3
15	400	7	180	1498	66.3	820	74.8

From the analysis, the control soil with no remediation had a concentration of 4446.34mg/kg and 3264.15mg/kg of Cr and Ni of respectively. According to the legislations and monitoring presented in the literature review, the amount of Cr and Ni allowed in soil is range is 0.05–3.950 (mg kg^{-1}) and the Regulatory limit is 100 (mg kg^{-1}) while 140mg/kg for Ni. Thus, it can be seen the amount of heavy metals found in this contaminated soil is really extremely higher than the allowed limit.

4.3.4 The Effect of Factors on Immobilization of Heavy Metals

From the table above, it can be observed biochar had the capacity to immobilize heavy metals and decrease it's concentration at to a maximum of 75.6 and 80.6 for Cr and Ni respectively. These results were obtained at the highest temperature of 500°C of biochar production while the lowest immobilization capacity of 61.0 and 60.5 for Cr and Ni respectively was observed at biochar production of 300°C. This shows the factor that had the highest effect was the temperature of biochar production. This result was attributed to the higher surface area and porosity of the biochar formed at the higher temperature. The increase in the pyrolysis temperature increasing the capacity of biomass to sorb heavy metal is a characteristic influence reported by Melo and coworkers who worked on revealing the capacity of this same biomass in heavy metal absorption with the effect of temperature[85].

Time had the second effect on immobilization of both metals showing the highest immobilization of Cromium and Nickel of 75.6% and 80.6% at the highest incubation time of 210days. This shows that as the time of contact of soil and biochar increases, the possible chance of immobilization is magnified. This effect of time on the remediation of soil was also absorbed in the research performed by Puga and collaborators assessing the ability of biochar on the immobilization of heavy metals by basing incubation as their factor[3].

Biochar dosage had the least effect showing a maximum immobilization percentage of 72.5% and 80.6% for Cromium and Nickel respectively. The effect of dosage has been studied by many researchers and it has repeatedly shown positive effect. This would clearly be due to the increased amount of biochar sites available for the immobilization of heavy metals from the surface of soil to the surface of biochar preceding it's being bioavalialbe to plants.

As for ash, the concentration of Cr and Ni in the remediated soil was found to be 197.01mg/kg and 323.4mg/kg showing immobilization 95.9% and 90.01% respectively. This shows ash has an extremely distinguished capacity to immobilize heavy metals from soil.

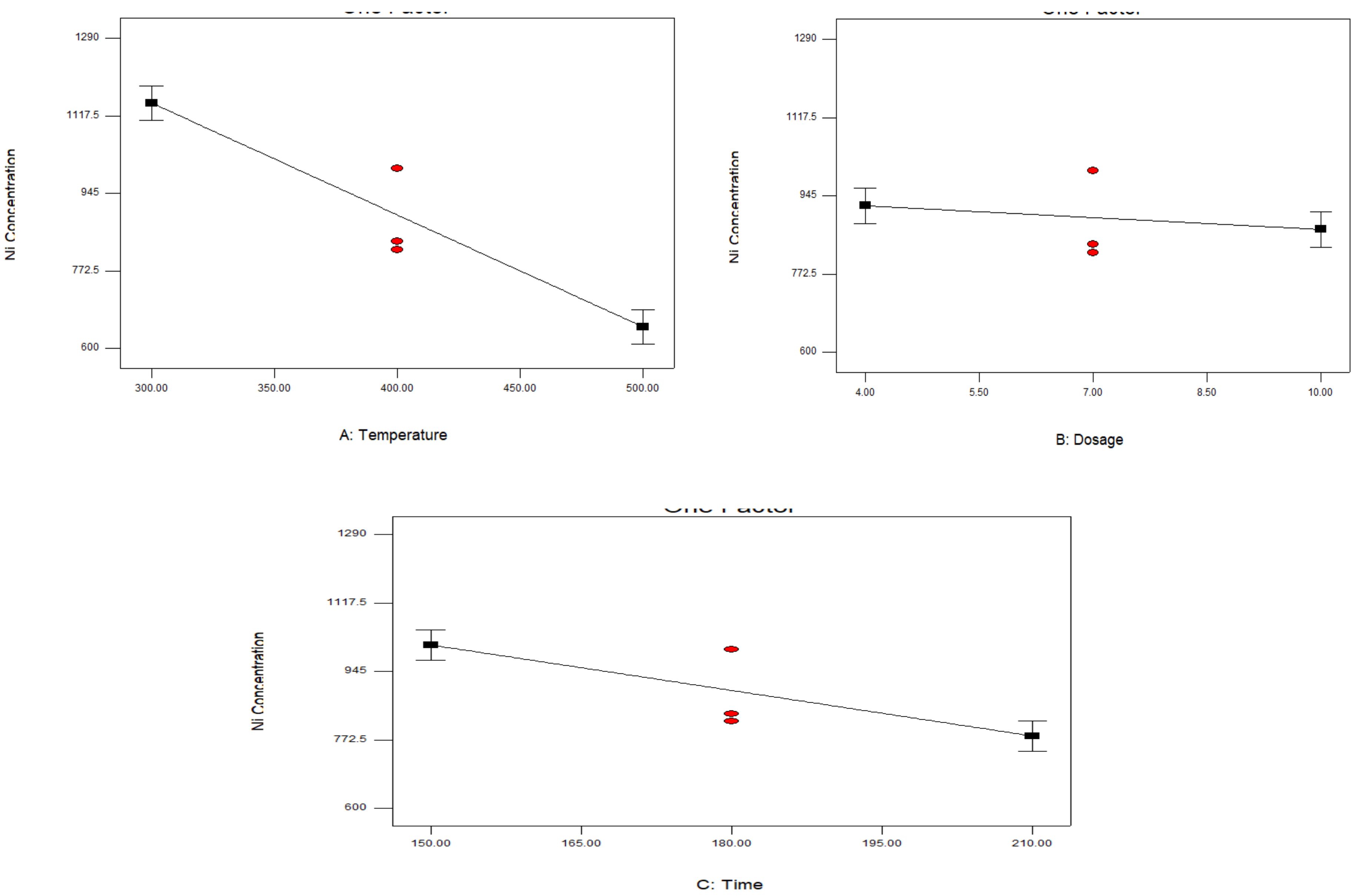


Figure 4.5: Effects of Factors on concentration of Nickel (a) Effect of Temperature, (b) Effect of Dosage and (c) Effect of Time

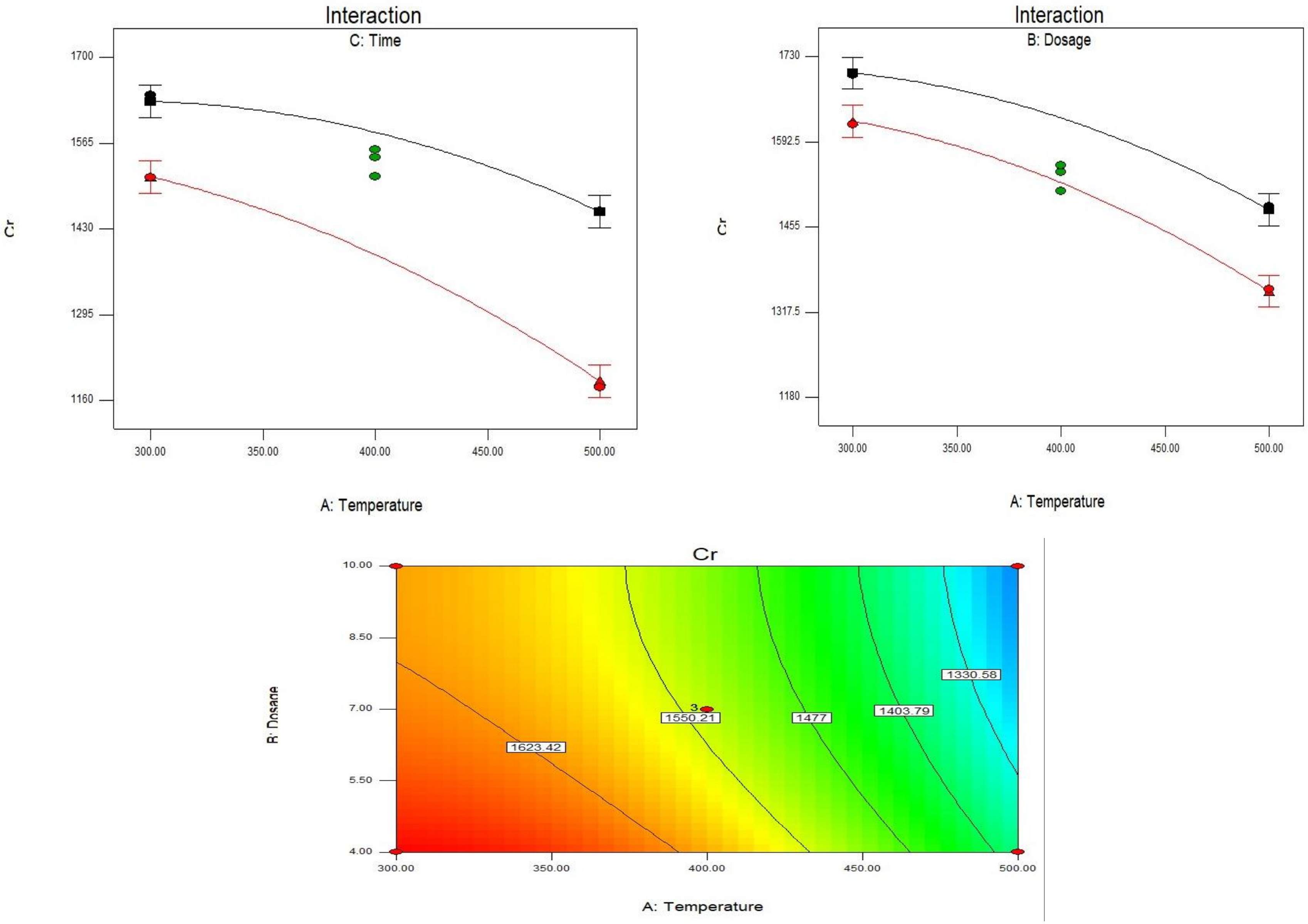


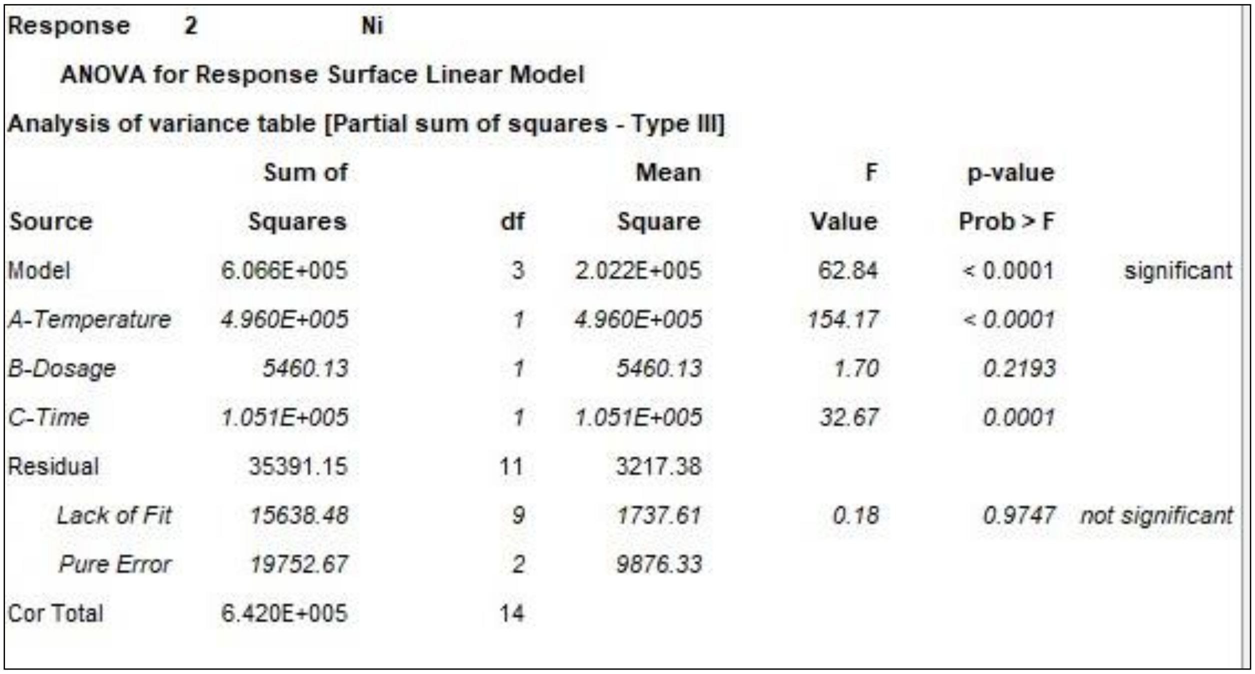
Figure 4.6: Effects of Factors on concentration of Chromium

4.4 Statistical Analysis

The adequacy of the model was checked by analysis of variance (ANOVA) and some diagnostic plots. Analysis of variance (ANOVA) is employed to test the significance of the developed models. The tests carried out to determine the adequate model were Sequential model Sum of Squares, Lack of Fit Tests and Model, Summary Statistics.

4.4.1 Statistical Analysis of Nickel Concentration

Table 4.11: ANOVA Response of Nickel



Response 2 Ni

ANOVA for Response Surface Linear Model

Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	6.066E+005	3	2.022E+005	62.84	< 0.0001	significant
A-Temperature	*4.960E+005*	*1*	*4.960E+005*	*154.17*	*< 0.0001*	
B-Dosage	*5460.13*	*1*	*5460.13*	*1.70*	*0.2193*	
C-Time	*1.051E+005*	*1*	*1.051E+005*	*32.67*	*0.0001*	
Residual	35391.15	11	3217.38			
Lack of Fit	*15638.48*	*9*	*1737.61*	*0.18*	*0.9747*	*not significant*
Pure Error	*19752.67*	*2*	*9876.33*			
Cor Total	6.420E+005	14				

If the model is a good prediction of their experimental results and the estimated factors effects are real. Also the high F-value and a very low probability indicates that the present models are in a good prediction of the experimental results. The p-value serves as a tool for checking the significance of each of the coefficients. The pattern of interaction between the variables is indicated by these coefficients. The variables with low probability levels contribute to the model, whereas the others can be neglected and eliminated from the model. Values of P>F less than 0.0500 indicates model terms are significant. Consequently, From the ANOVA response table on nickel above, it is seen that temperature and time independently has the highest significant effect on the result but the interaction effect of any of the factors doesn’t seem to show any significance. It was found that linear model was the most suitable fit for the present study than quadratic model and was the highest order where the additional terms were significant as the value of cubic model could not be defined in the Model Summary Statistics for all responses. In addition, it can be observed that linear model had the highest p-value for Lack of Fit Tests. The final equation is shown as follows

Nickel Concentration = 896.8 – 249A – 26.12B – 114.63C

Where A – Temperature B - Dosage and C - Time

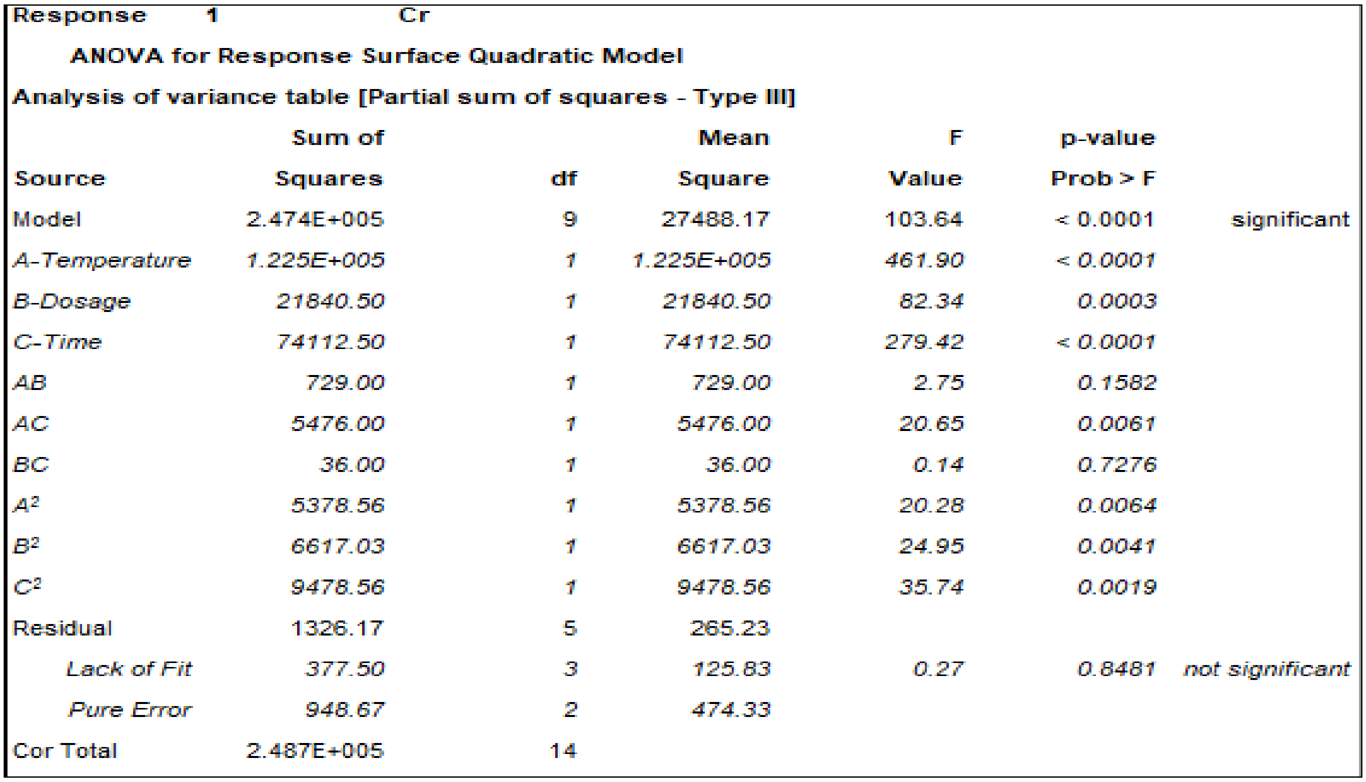
The regression coefficients of the developed model are determined from the regression analysis. Also the regression value is between [0,1], and as it approaches to 1, it fits well to the experimental data otherwise it indicates failure of approximation. R was observed to be 0.98 which is closer to one and is good fit. In addition, The "Pred R-Squared" of 0.9131 is in reasonable agreement with the "Adj R-Squared" of 0.9298. "Adeq Precision" measures the signal to noise ratio.

For the evaluation of normality of the residuals, a graphical visualization of the normal probability plot is considered as the proper method. Normal plot of residuals graph is a technique for assessing whether or not a data set is approximately normally distributed. The experimental data were plotted against a theoretical normal distribution in such a way that points should form approximate straight-line. For this specific response, It can be observed that, the data are spread approximately in a straight line, which show a good correlation between experimental and predicted values for the responses. The plots can be found in Appendix E.2.

Running a regression analysis, the variance of the error terms must be constant and they must have a mean of zero. If this is not the case, the model may not be valid. In this response, the points on the plot appear to be randomly scattered around zero so assuming that error terms had a mean of zero was reasonable. The vertical width of the scatter does not appear to increase or decrease across the fitted values. The plots of observed versus predicted values shows minimal variation between the observed and fitted values for all responses, All plots are presented in Appendix E.2. ANOVA and analysis of residual plots for the three responses, the model does not reveal inadequacy.

4.4.2 Statistical Analysis of Cromium Concentration

Table 4.12: ANOVA Response of Cromium



Response 1 Cr

ANOVA for Response Surface Quadratic Model

Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	2.474E+005	9	27488.17	103.64	< 0.0001	significant
A-Temperature	*1.225E+005*	*1*	*1.225E+005*	*461.90*	*< 0.0001*	
B-Dosage	*21840.50*	*1*	*21840.50*	*82.34*	*0.0003*	
C-Time	*74112.50*	*1*	*74112.50*	*279.42*	*< 0.0001*	
AB	*729.00*	*1*	*729.00*	*2.75*	*0.1582*	
AC	*5476.00*	*1*	*5476.00*	*20.65*	*0.0061*	
BC	*36.00*	*1*	*36.00*	*0.14*	*0.7276*	
A^2	*5378.56*	*1*	*5378.56*	*20.28*	*0.0064*	
B^2	*6617.03*	*1*	*6617.03*	*24.95*	*0.0041*	
C^2	*9478.56*	*1*	*9478.56*	*35.74*	*0.0019*	
Residual	1326.17	5	265.23			
Lack of Fit	*377.50*	*3*	*125.83*	*0.27*	*0.8481*	*not significant*
Pure Error	*948.67*	*2*	*474.33*			
Cor Total	2.487E+005	14				

According to the ANOVA response of Cromium all the models are significant while time and tempreature are the most significant. The interaction effect of time and tempreture shows significnce with a value of 0.0061<0.05. . It was found that quadratic model was the most suitable fit for the present as it had the highest p-value for Lack of Fit Tests. The final equation is shown as follows

$$\text{Chromium Concentration} = 1536.33 - 123.75A - 52.25B - 96.25C - 13.5AB - 37AC - 37AC - 3BC - 38.17A^2 + 42.33B^2 - 50.67C^2$$

R was observed to be 0.9947 which is closer to one and is good fit. In addition, The "Pred R-Squared" of 0.9671 is in reasonable agreement with the "Adj R-Squared" of 0.9851. Regarding the Normal probability plot, It can be observed that, the data are spread approximately in a straight line, which show a good correlation between experimental and predicted values for the responses.

In addition, it can be observed that, the data are spread approximately in a straight line, which show a good correlation between experimental and predicted values for the responses. As presented in Appendix E.1, all the dignositic plots are in agreement and don't indicate anything unusual about the model. Thus, ANOVA and analysis of residual plots for the three responses, the model does not reveal inadequacy.

4.4.3 Optimization of Process Parameters

In order to identify the optimum conditions, desirability function was used to identify the optimum levels of factors and to get maximum desirable responses. The program combines individual desirability into a single number and then searches for the greatest overall desirability. A value of one represents the ideal case. In order to determine the optimum processing conditions, the temperature and time ranges were maximized while dosage was held to be "in range". The optimization solution of this model showed the selected or best results of immobilization would be gained at the temperature of 500°C, Dosage of 8.83% and time of 210 days. At this selected point the concentration of Nickel was found to be 517.21 and Chromium 1164.3.

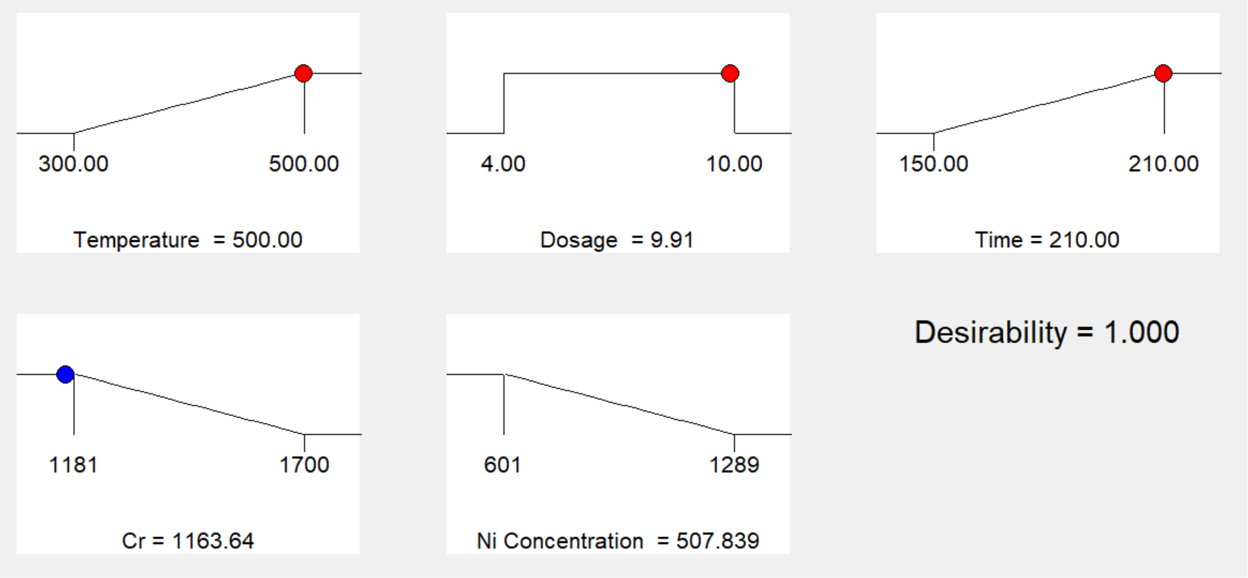


Figure 4.7: Ramp plots of optimization solution for the responses

5. CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

This study focused on analyzing the capacity of sugar cane straw derived biochar and ash for the remediation of soil which has been contaminated by heavy metals specifically Cr and Ni from the effluent of Electroplating Industry. The proximate analysis of sugarcane straw biomass showed low moisture content (7.1%), low ash content (1.74%) and high volatile matter (85.4%). These results are typically what is generally expected of biomass that is going to be used for the purpose of soil remediation. Sugar cane straw was used for the production of biochar using the pyrolysis process by the variation of temperature ranging from 300 to 500 degrees at a constant rate and residence time of 10°C/min and 1hr respectively. In addition, Ash was produced in a muffle furnace at a temperature of 700degrees. During this carbonization process the highest yield was obtained at the lowest temperature of 300°C (50%) while ash showed a yield of 31.6%.

Biochar was characterized using different methods for the analysis of its capacity to immobilize heavy metals from contaminated soil prior to application. These characterizations include proximate analysis, MB absorption capacity, Exchangeable Bases and CEC, Heavy metal content, FTIR spectroscopy and pH and EC. The proximate analysis performed on BC showed good results. Moreover, these results seem to increase with the severity of pyrolysis process indicating the quality of BC produced. The ultimate analysis showing BC to be quite carbonaceous (67.18%) pointing out its capacity to sequester carbon in soil. In addition the ratio of H/C (0.54) shows its aromacity related to its organic content showing good stability in soil. All these disclose the variety of beneficial features of biochar properties.

The results from these methods showed that biochar produced from this specific biomass possesses the typical functional groups that enable it to store carbon, the appropriate pH and EC that could remediate acidic and saline soil respectively, a fine amount of macro and micro nutrients that would aid plant growth. Methylene Blue absorption indicates the surface area and pore structure of BC which showed a notable absorption capacity which indicates its ability to immobilize heavy metals from soil. This result increase with severity of temperature showing higher temperature activates the pores of BC enabling it immobilize more element on its surface.

This result was attributed to the chemical structure of the biochars as well as physical structures such as BET surface areas, particularly internal surface areas. The heavy metal analysis of BC showed the contents were below detection limit thus posing no risk for soil. CEC analysis of 29Meq/100g presented an expected effective nutrient addition capacity of BC to soil. The pH value of BC showed its basic character which is one of its typical behaviors. The increase in temperature increased this property. This basic character increased the acidity of soil (4.8) to a maximum value of 6.8 at a dosage of 10%w/w and incubation time of 150days and 7.5 for ash remediation. The FTIR spectra showed the characteristic C-H stretch showing its organic nature and carboxyl C=O stretch and aromatic C= C stretches. The increase in temperature showed the increase in these stretches showing the decrease in stability of BC.

The application of BC significantly decreased concentration of Cr and Ni to 75.6 and 80.6 respectively in soil by immobilization to the surface of BC. From the results, it can be concluded the BC produced with higher amount of temperature possess better capacity of immobilization. In addition the increase in dosage and incubation time facilitates the immobilization process. The CEC value of remediated soil was found to be 29.9Meq/100g. The most noteworthy effect detected was from biochar produced at the highest temperature. In addition, Ash was discovered to have an extreme immobilization ability reaching 95.5% immobilization of Cr and 90.5 of Ni.

All in all, sugar cane straw BC was found to be a fine soil remediating material possessing all the necessary properties for the immobilization of heavy metal contaminants and making available an abundance of nutrients while ash displayed an outstanding liming effect and an exceptional immobilization ability.

5.2. Recommendations

Due to certain limitations, this study only focused on the immobilization capacity of Sugar cane straw biochar by decreasing the concentration of Cr and Ni from the surface of contaminated soil. Further studies on the capacity of this biochar needs to be performed by application of bioavailability studies through conducting different plant growth experiments and studying the concentration of heavy metals on their pore water, root and shoots.

Although this study mainly focused on the capacity of Sugarcane straw BC for the remediation of heavy metal contaminated soil, the small number of methods used to check its capacity to increase soil nutrients, it showed positive results. Thus, more studies need to be performed to analyze the additional capacity of this specific biomass for the increase of plant available nutrients leading to the increased productivity of crops.

In addition, as a result of a few limitations discussed, this research was not conducted to its fullest capacity. Thus, better results can be obtained by using an authentic contaminated soil other than an artificially prepared one and with advanced budget accessibility a various set of characterizations can be performed to better exploit the hidden ability of this biomass in regards to contaminated soil and water remediation.

As far as the use of Sugar cane straw ash is concerned, this study has shown an introduction to the capacity of ash for the immobilization of heavy metals and its liming effect considering the heavy metal content and pH of remediated soil. As it has been discussed above, these results proved to be quite outstanding. This invites further study to be carried out applying ash and investigating its different physical and chemical properties that would unlock its numerous hidden capabilities.

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APPENDICES

Appendix A - Calculations

Appendix A.1 Sample Proximate Analysis Calculations

Moisture content determination

Weight of sample before drying (W_1) = 30 g

Weight of sample after drying (W_2) = 26.31 g

$$\text{Moisture content} = \frac{W_1\text{-}W_2}{W_2}*100$$

$$\text{Moisture content} = \frac{30\text{-}27.90}{27.90}*100$$

$$= 7.1\%$$

Volatile Matter Determination

Weight of crucible =15.73 g

Weight of crucible and sample before incineration (W_1) = 16.83 g

Weight of crucible and sample after incineration (W_2) = 15.89 g

$$\text{volatile solids} = \frac{W_1\text{-}W_2}{W_1}*100$$

$$\text{volatile solids} = \frac{1.1\text{-}0.6}{1.1}*100$$

$$= 85.4\%$$

Ash Content Determination

Weight of crucible (Wc) = 28.93

Weight of crucible and sample before incineration (W_1) = 31.23g

Weight of crucible and sample after incineration (W_2) = 28.97 g

$$\text{Ash content} = \frac{W_1\text{-}W_c}{W_2\text{-}W_c}*100$$

$$= \frac{(28.97 - 28.93)}{(31.23 - 28.93)} \times 100$$

$$= 1.73\%$$

Fixed Carbon Determination

$$FC = 100 - (\%M + \%A + \%V)$$

$$FC = 100 - (7.5 + 85.4 + 1.73)$$

$$= 5.37\%$$

Bulk Density Determination

$Bulk\ Density\ (kg/m3) = mass\ of\ sample\ (kg)/\ volume\ of\ sample\ (m3)$

= 4.36g/19ml

= 0.3g/ml

Bulk Density Determination

$Bulk\ Density\ (kg/m3\ ) = mass\ of\ sample\ (kg)/\ volume\ of\ sample\ (m3)$

= 4.36g/19ml

= 0.3g/ml

Appendix A.2 Ultimate Value and Yield Calculation of Biochar

C/H value Calculation

$$\frac{H}{C} = \frac{\dfrac{\text{Weight Percent Hydrogen}}{\text{Atomic Weight Hydrogen}}}{\dfrac{\text{Wight percent Carbon}}{\text{Atomic Weight Carbon}}}$$

$$= \frac{(2.77/\ 1.008)}{(61.18/\ 12.011)}$$

$$= 0.54$$

Biochar and Ash Yield Calculation

Yield (%) = (Weight of Biochar) / (Weight of Feedstock) × 100

300^0C

Yield (%) = (Weight of Biochar) / (Weight of Feedstock) × 100

Yield (%) = (40g) / (80g) × 100 = 50%

Percentage Removal and Adsorption Capacity Calculations

BC300

$$q(mg/g) = \frac{(\ Co - C\ ).V}{m}$$

$$= \frac{(150 - 114.78) \,.\, 0.05\text{L}}{0.1 \text{ g}} = 17.61\text{mg/g}$$

$$\text{MB Removal \%} = \frac{(\text{Co} - \text{C1})}{\text{Co}} \times 100$$

$$= \frac{(150 - 114.78)}{150} \times 100 = 23.48\%$$

Appendix B Calibration Curve used for Determination of MB concentration

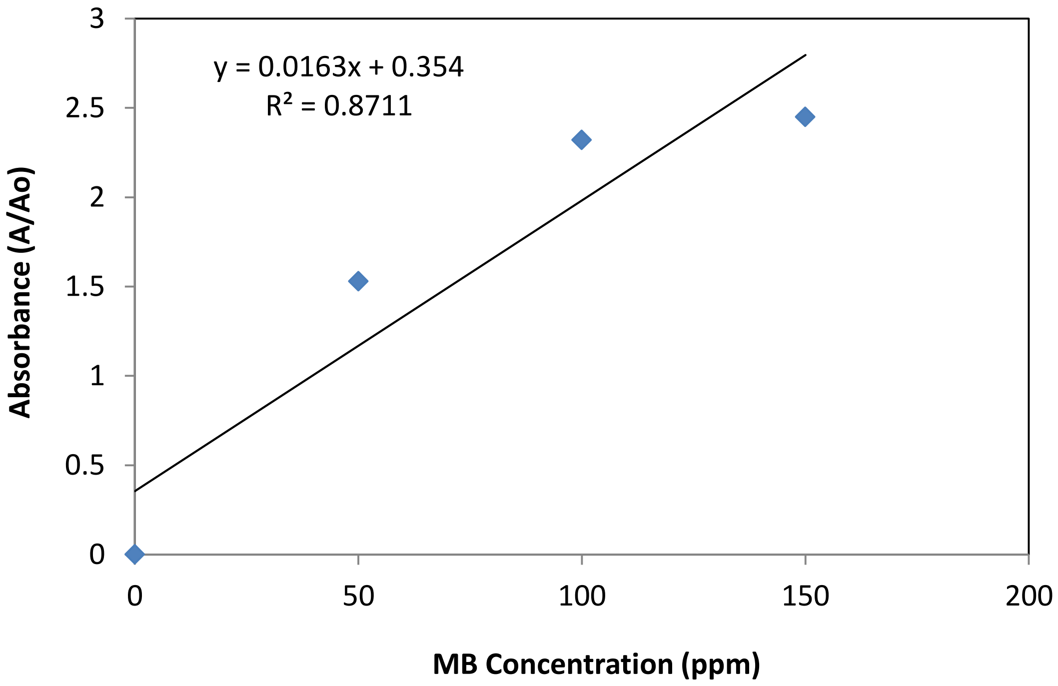


Figure B.1: Calibration curve for determination of MB concentration

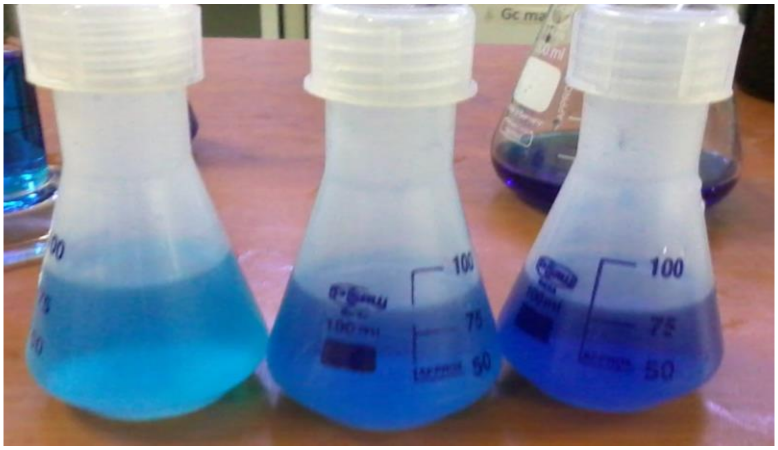
Appendix C. Laboratory Pictures

Picture C.1: Biochar produced through pyrolysis

Picture C.2: Ash produced using muffle furnace

Picture C.3: Pyrolysis Equipment Setup

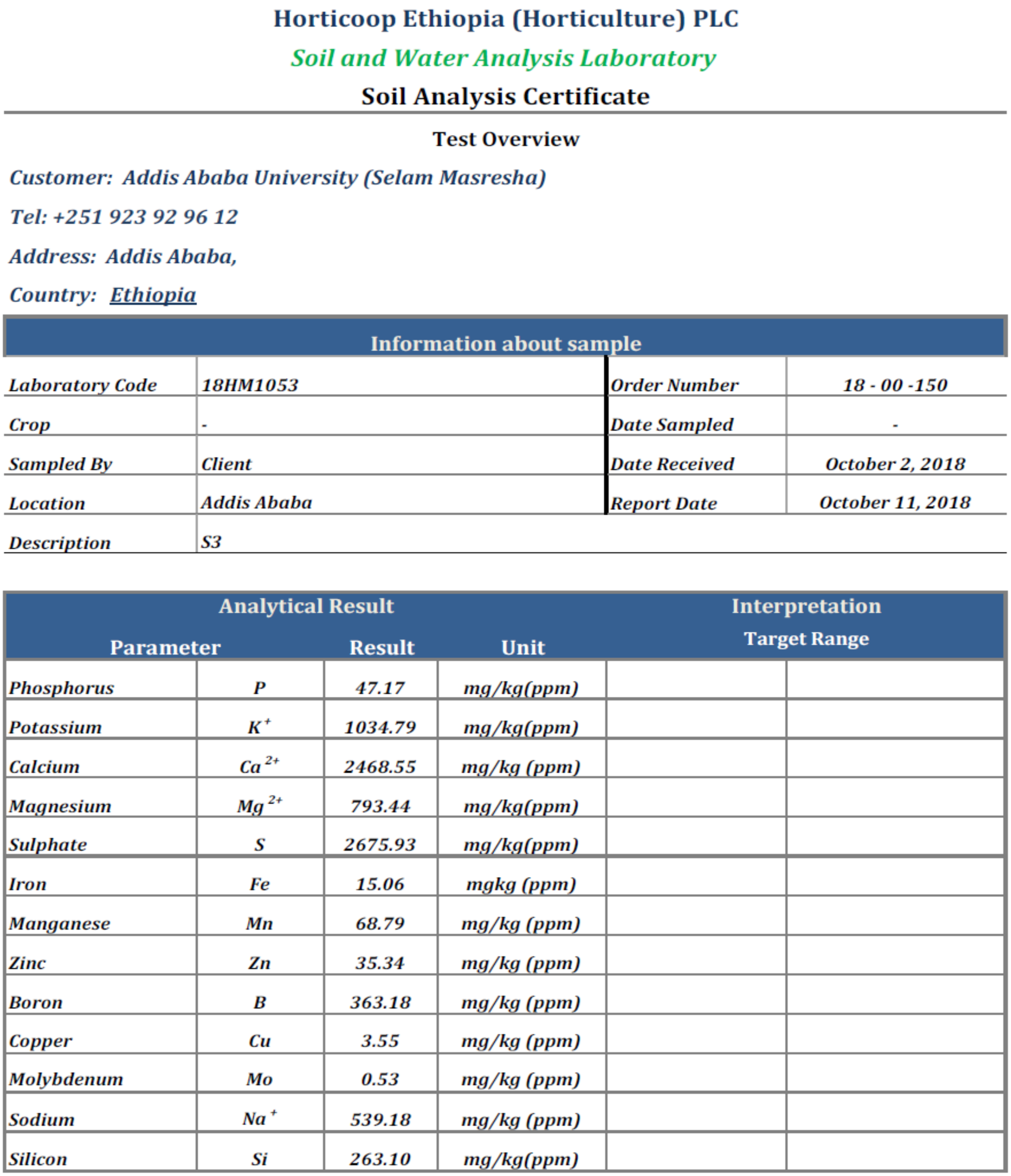
Picture C.4: Contaminated soil with remediation in incubation pots



Picture C.5: Biochar absorption determination using Methylene Blue

Appendix D Results of Heavy Metal and CEC Analysis

Table D.1: Heavy metal and CEC analysis of sample



Horticoop Ethiopia (Horticulture) PLC

Soil and Water Analysis Laboratory

Soil Analysis Certificate

Test Overview

Customer: Addis Ababa University (Selam Masresha)

Tel: +251 923 92 96 12

Address: Addis Ababa,

Country: Ethiopia

Information about sample			
Laboratory Code	*18HM1053*	*Order Number*	*18 - 00 -150*
Crop	*-*	*Date Sampled*	*-*
Sampled By	*Client*	*Date Received*	*October 2, 2018*
Location	*Addis Ababa*	*Report Date*	*October 11, 2018*
Description	*S3*		

Analytical Result				Interpretation	
Parameter		Result	Unit	Target Range	
Phosphorus	*P*	*47.17*	*mg/kg(ppm)*		
Potassium	*K^+*	*1034.79*	*mg/kg(ppm)*		
Calcium	*Ca^{2+}*	*2468.55*	*mg/kg (ppm)*		
Magnesium	*Mg^{2+}*	*793.44*	*mg/kg(ppm)*		
Sulphate	*S*	*2675.93*	*mg/kg(ppm)*		
Iron	*Fe*	*15.06*	*mgkg (ppm)*		
Manganese	*Mn*	*68.79*	*mg/kg (ppm)*		
Zinc	*Zn*	*35.34*	*mg/kg (ppm)*		
Boron	*B*	*363.18*	*mg/kg (ppm)*		
Copper	*Cu*	*3.55*	*mg/kg (ppm)*		
Molybdenum	*Mo*	*0.53*	*mg/kg (ppm)*		
Sodium	*Na^+*	*539.18*	*mg/kg (ppm)*		
Silicon	*Si*	*263.10*	*mg/kg(ppm)*		

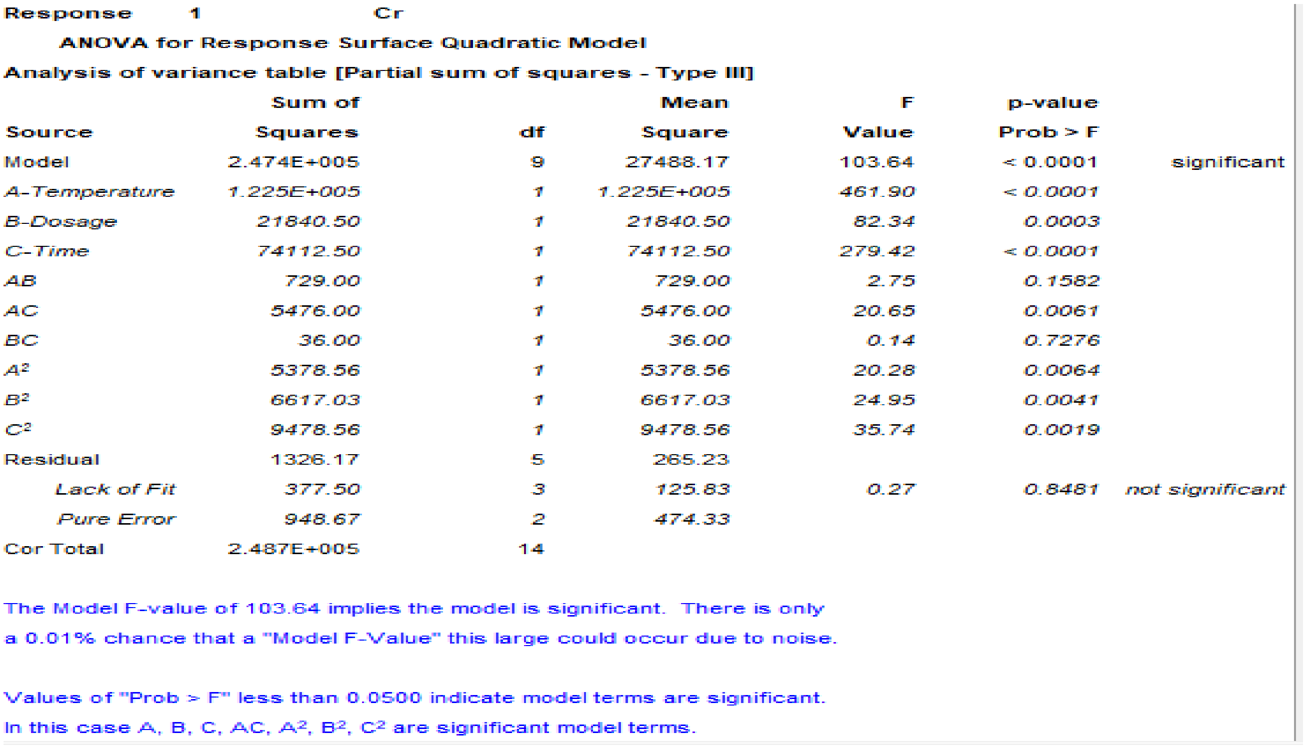
Analytical Result				**Interpretation**	
Parameter		**Result**	**Unit**	**Target Range**	
Merrcury	*Hg*	*0.21*	*mg/kg(ppm)*	-	-
Chromium	*Cr*	*1,081.79*	*mg/kg(ppm)*	-	-
Cadimium	*Cd*	*0.10*	*mg/kg(ppm)*	-	-
Tin	*Sn*	*1.50*	*mg/kg(ppm)*	-	-
Arsenic	*As*	*0.96*	*mg/kg(ppm)*	-	-
Nicol	*Ni*	*724.91*	*mg/kg(ppm)*	-	-
Lead	*Pb*	*0.33*	*mg/kg(ppm)*	-	-
Cation Exchange Capacity		*29.20*	*Meq/100g soil*	*15 – 25*	*High*

Analytical Methods		
Parameter	***Examination Standards***	
Cation Exchange Capacity	*CEC*	*Ammonium Acetate Method*
Calcium (Ca), Potassium (K), Magnesium (Mg),		
Sulfur (S),Silicon (Si),Molybdenum (Mo), and Boron (B)		
Copper (Cu), Iron (Fe), Manganese (Mn)and Zinc (Zn)		
Mercury,Arsenic(As)Nickle(Ni)Cobalt (Co)Lead(Pd)Chromium(Cr)		*Mehlich-3*

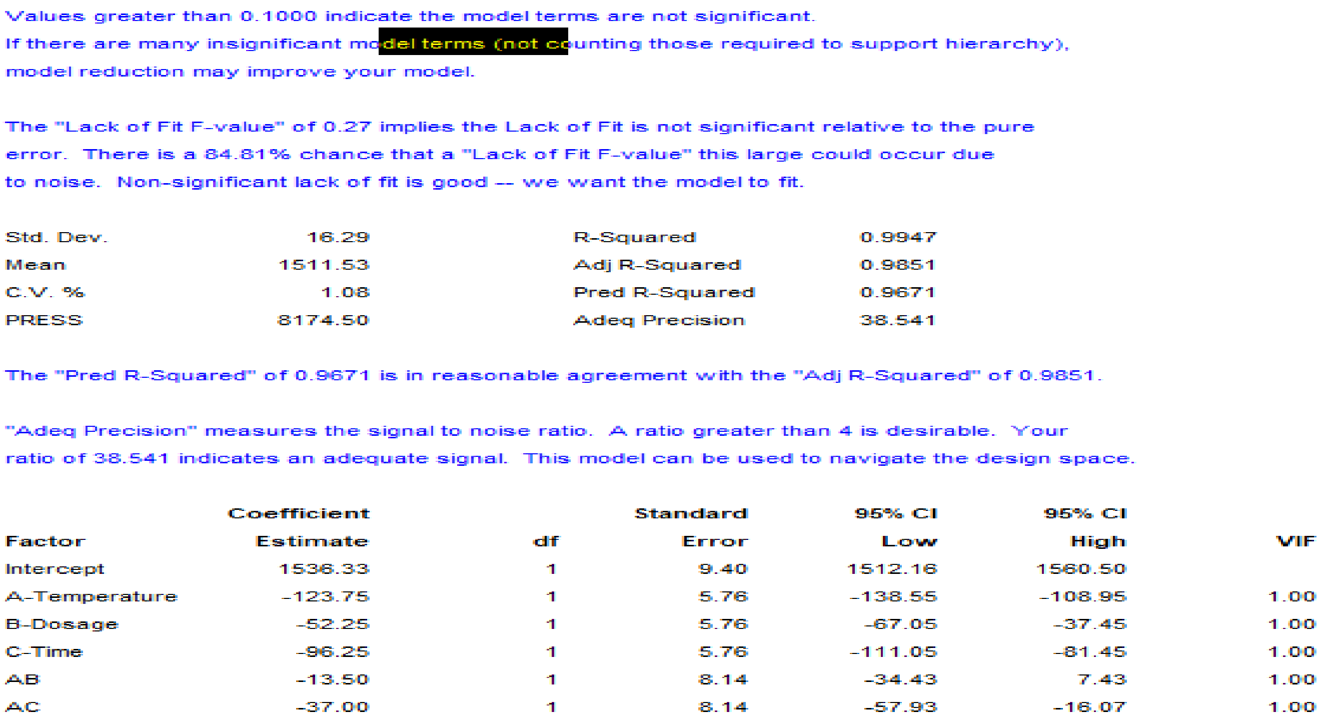
Appendix E. Design Expert Output

Appendix E.1 Anova Tables

Table E.1 ANOVA Table of Response Chromium Concentration

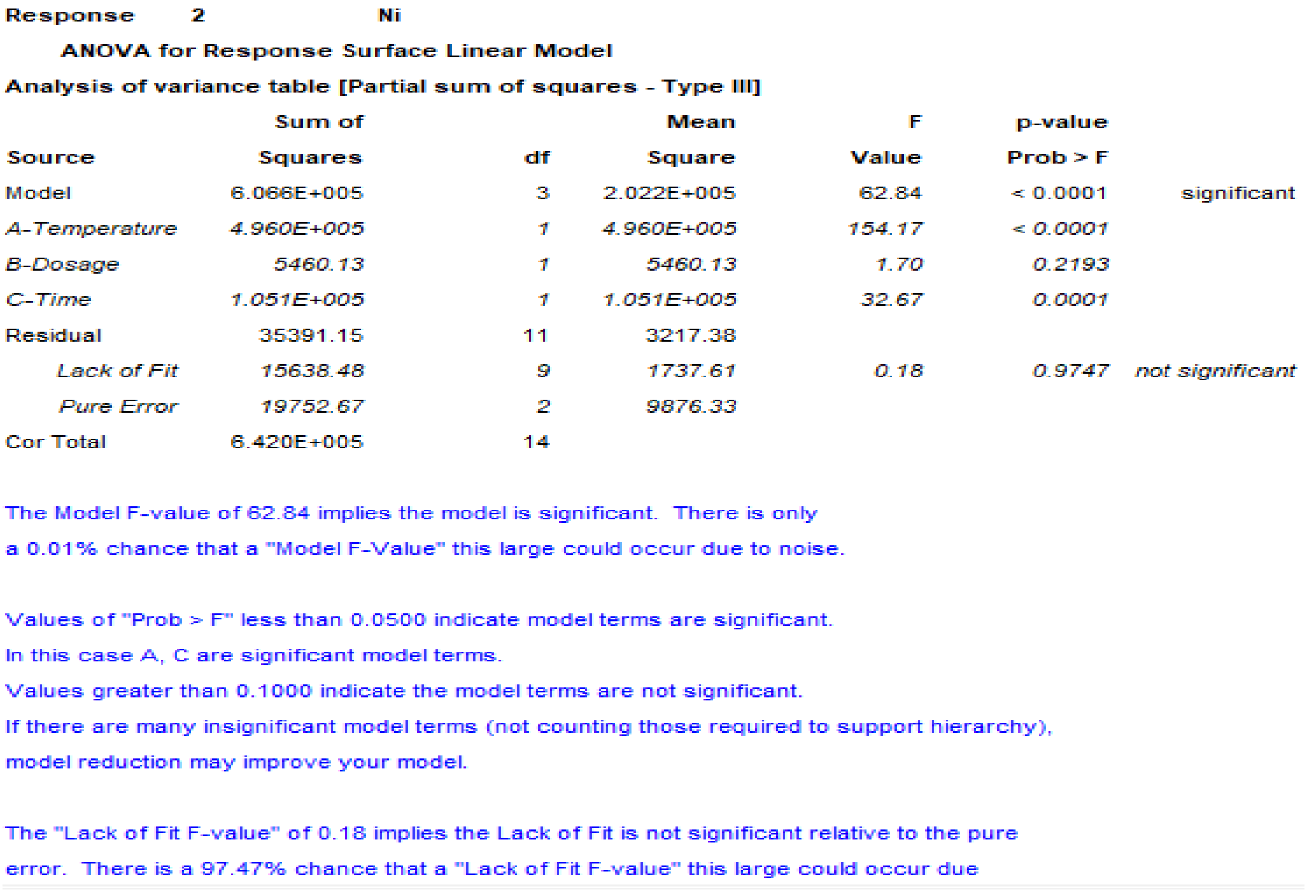


```
Response         1                 Cr
      ANOVA for Response Surface Quadratic Model
Analysis of variance table [Partial sum of squares - Type III]
                          Sum of                           Mean           F        p-value
Source                  Squares            df            Square       Value       Prob > F
Model                 2.474E+005            9          27488.17      103.64       < 0.0001       significant
A-Temperature         1.225E+005            1        1.225E+005      461.90       < 0.0001
B-Dosage                21840.50            1          21840.50       82.34         0.0003
C-Time                  74112.50            1          74112.50      279.42       < 0.0001
AB                        729.00            1            729.00        2.75         0.1582
AC                       5476.00            1           5476.00       20.65         0.0061
BC                         36.00            1             36.00        0.14         0.7276
A²                       5378.56            1           5378.56       20.28         0.0064
B²                       6617.03            1           6617.03       24.95         0.0041
C²                       9478.56            1           9478.56       35.74         0.0019
Residual                 1326.17            5            265.23
     Lack of Fit          377.50            3            125.83        0.27         0.8481   not significant
     Pure Error           948.67            2            474.33
Cor Total             2.487E+005           14

The Model F-value of 103.64 implies the model is significant.  There is only
a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant.
In this case A, B, C, AC, A², B², C² are significant model terms.
```

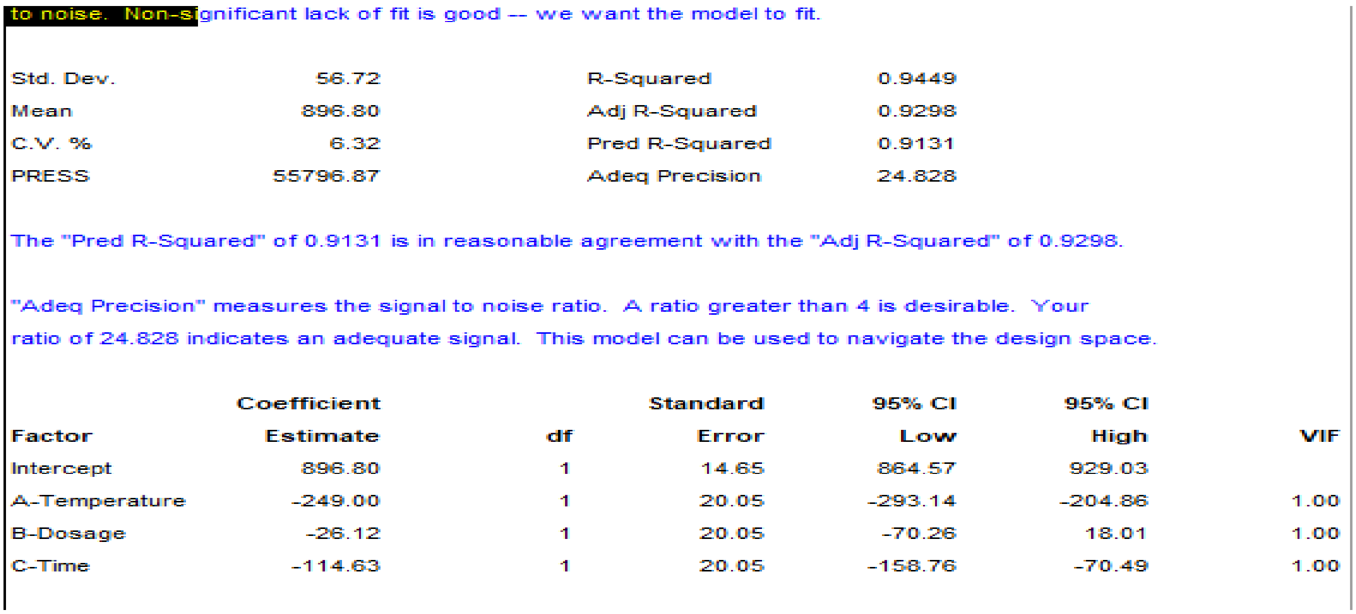


```
Values greater than 0.1000 indicate the model terms are not significant.
If there are many insignificant model terms (not counting those required to support hierarchy),
model reduction may improve your model.

The "Lack of Fit F-value" of 0.27 implies the Lack of Fit is not significant relative to the pure
error.  There is a 84.81% chance that a "Lack of Fit F-value" this large could occur due
to noise.  Non-significant lack of fit is good -- we want the model to fit.

Std. Dev.                16.29             R-Squared             0.9947
Mean                   1511.53             Adj R-Squared         0.9851
C.V. %                    1.08             Pred R-Squared        0.9671
PRESS                  8174.50             Adeq Precision        38.541

The "Pred R-Squared" of 0.9671 is in reasonable agreement with the "Adj R-Squared" of 0.9851.

"Adeq Precision" measures the signal to noise ratio.  A ratio greater than 4 is desirable.  Your
ratio of 38.541 indicates an adequate signal.  This model can be used to navigate the design space.

                     Coefficient                   Standard       95% CI        95% CI
Factor                  Estimate       df             Error          Low          High          VIF
Intercept                1536.33        1              9.40      1512.16       1560.50
A-Temperature            -123.75        1              5.76      -138.55       -108.95         1.00
B-Dosage                  -52.25        1              5.76       -67.05        -37.45         1.00
C-Time                    -96.25        1              5.76      -111.05        -81.45         1.00
AB                        -13.50        1              8.14       -34.43          7.43         1.00
AC                        -37.00        1              8.14       -57.93        -16.07         1.00
```

Table E.2 ANOVA Table of Response 2 Nickel Concentration



```
Response        2                 Ni
      ANOVA for Response Surface Linear Model
Analysis of variance table [Partial sum of squares - Type III]
                      Sum of                        Mean           F        p-value
Source               Squares          df          Square       Value       Prob > F
Model              6.066E+005          3      2.022E+005       62.84       < 0.0001      significant
A-Temperature      4.960E+005          1      4.960E+005      154.17       < 0.0001
B-Dosage              5460.13          1         5460.13        1.70         0.2193
C-Time             1.051E+005          1      1.051E+005       32.67         0.0001
Residual             35391.15         11         3217.38
   Lack of Fit       15638.48          9         1737.61        0.18         0.9747   not significant
   Pure Error        19752.67          2         9876.33
Cor Total          6.420E+005         14

The Model F-value of 62.84 implies the model is significant.  There is only
a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant.
In this case A, C are significant model terms.
Values greater than 0.1000 indicate the model terms are not significant.
If there are many insignificant model terms (not counting those required to support hierarchy),
model reduction may improve your model.

The "Lack of Fit F-value" of 0.18 implies the Lack of Fit is not significant relative to the pure
error.  There is a 97.47% chance that a "Lack of Fit F-value" this large could occur due
```



```
to noise.  Non-significant lack of fit is good -- we want the model to fit.

Std. Dev.            56.72              R-Squared          0.9449
Mean                896.80              Adj R-Squared      0.9298
C.V. %                6.32              Pred R-Squared     0.9131
PRESS             55796.87              Adeq Precision     24.828

The "Pred R-Squared" of 0.9131 is in reasonable agreement with the "Adj R-Squared" of 0.9298.

"Adeq Precision" measures the signal to noise ratio.  A ratio greater than 4 is desirable.  Your
ratio of 24.828 indicates an adequate signal.  This model can be used to navigate the design space.

               Coefficient                 Standard       95% CI       95% CI
Factor            Estimate        df          Error          Low         High          VIF
Intercept           896.80         1          14.65       864.57       929.03
A-Temperature      -249.00         1          20.05      -293.14      -204.86         1.00
B-Dosage            -26.12         1          20.05       -70.26        18.01         1.00
C-Time             -114.63         1          20.05      -158.76       -70.49         1.00
```

Appendix E.2 Diagnostic Plots

E.2.1 Diagnostic Plots of Response 1(Chromium Concentration)

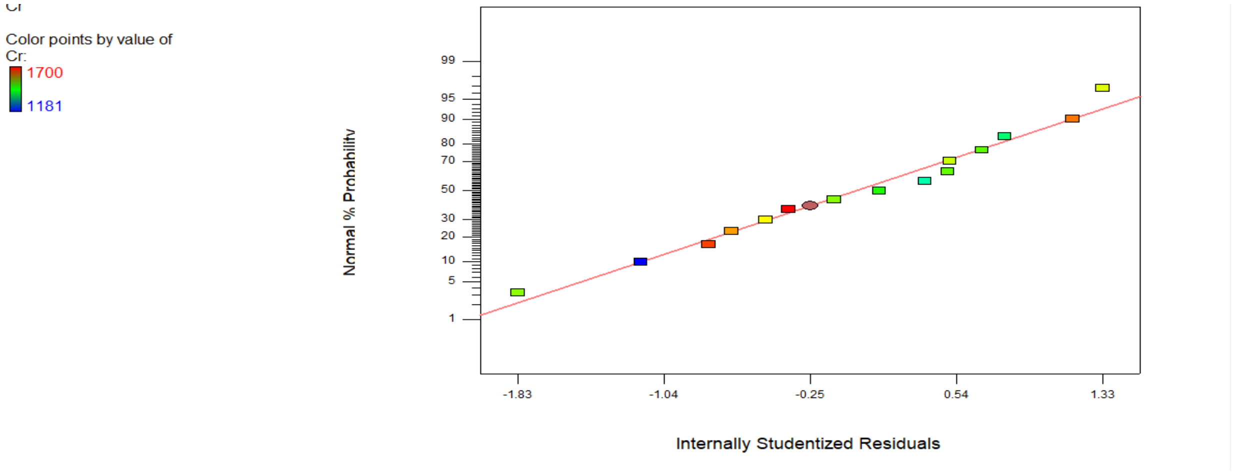


Figure E-1: Normal Plot of Residuals

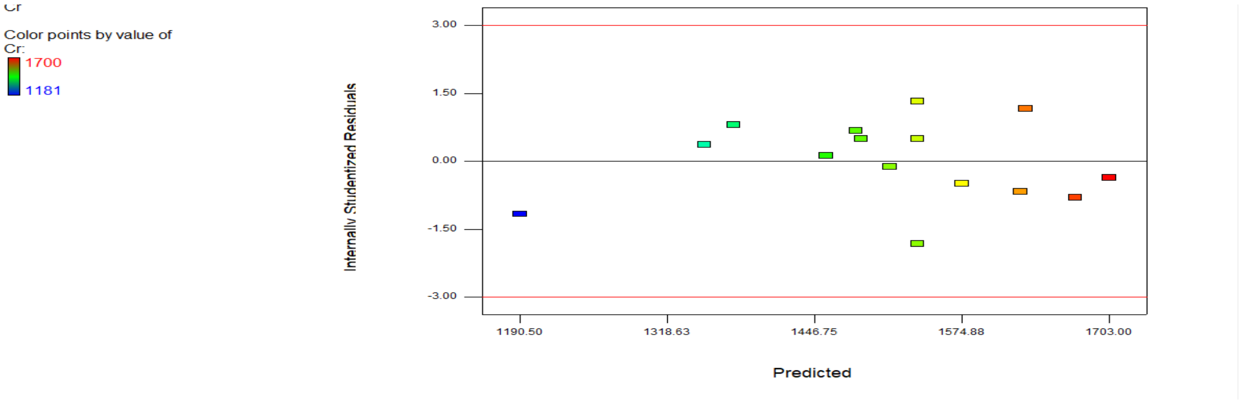


Figure E -2: Plot of Residuals Vs. Predicted Values

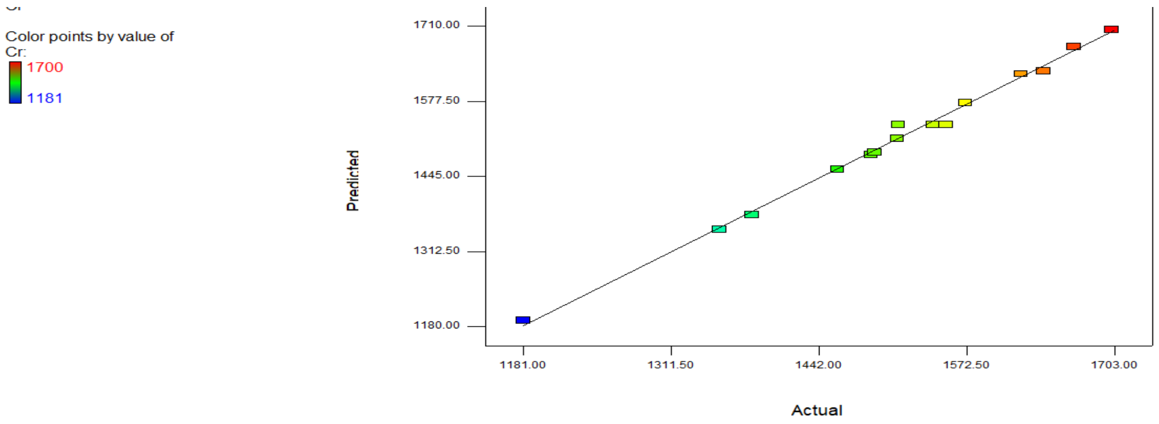


Figure E-3: Plot of Predicted Vs. Actual Values

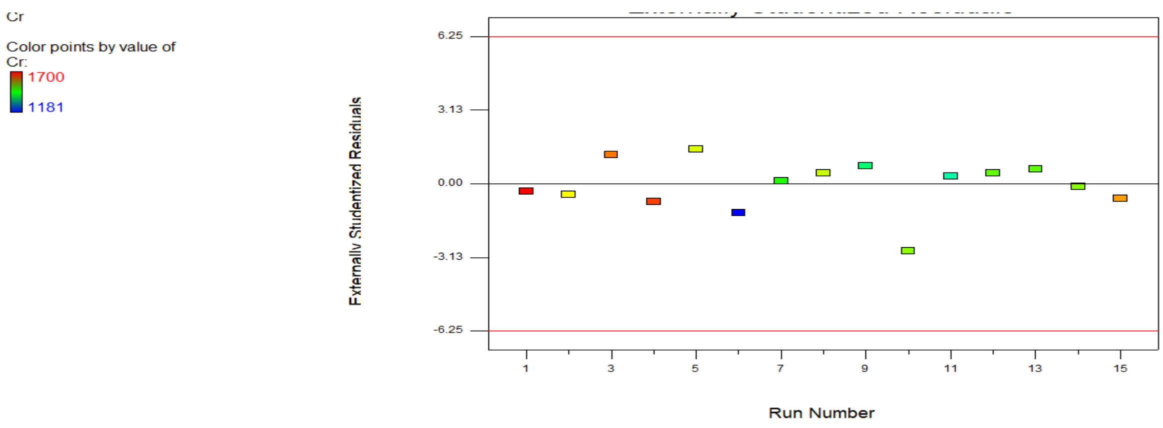


Figure E-4: Plot of Externally Studentized Residuals

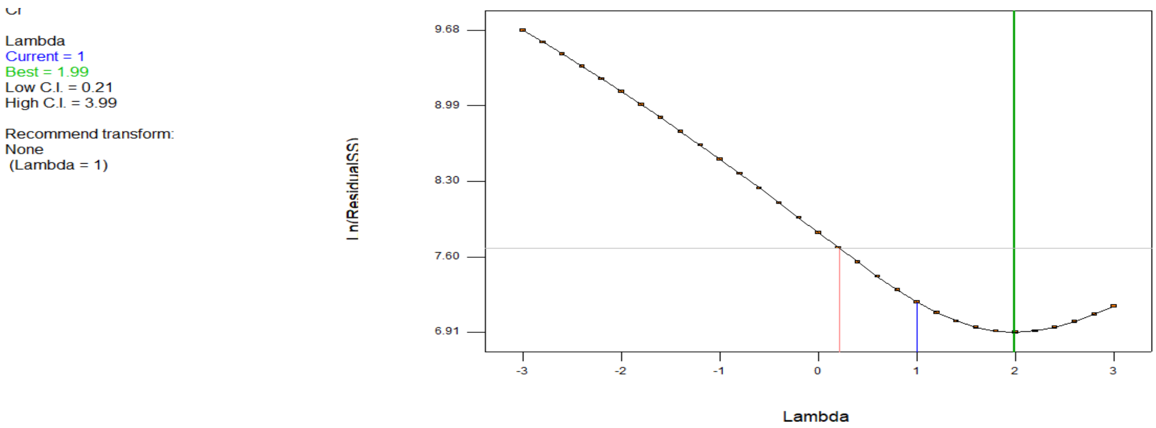


Figure E-5: Box – Cox plot For power Transforms

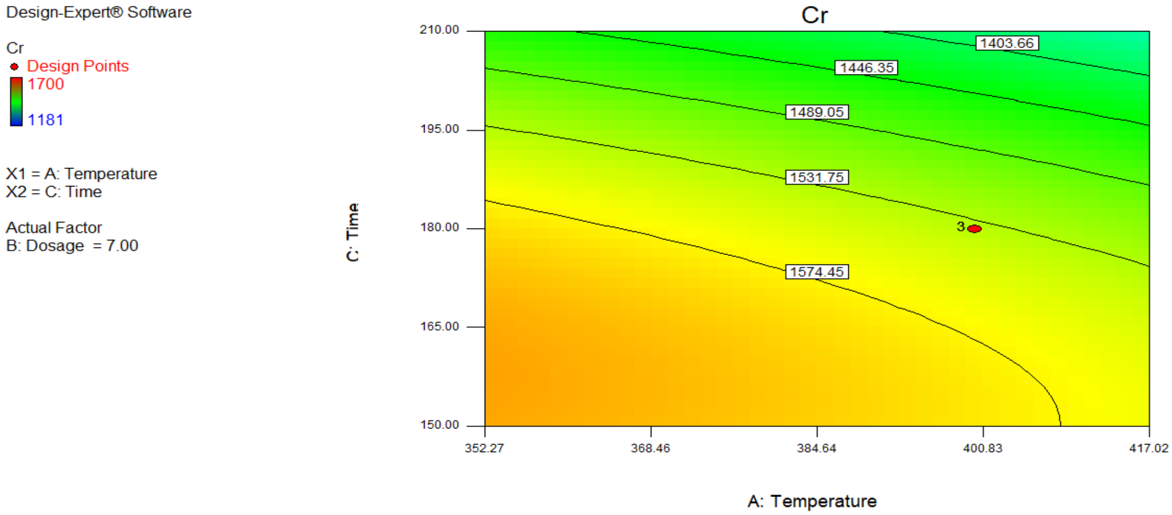


Figure E-6: Contour Graph of Temperature and Time interaction

E.2.2 Diagnostic Plots of Response 2(Nickel Concentration)

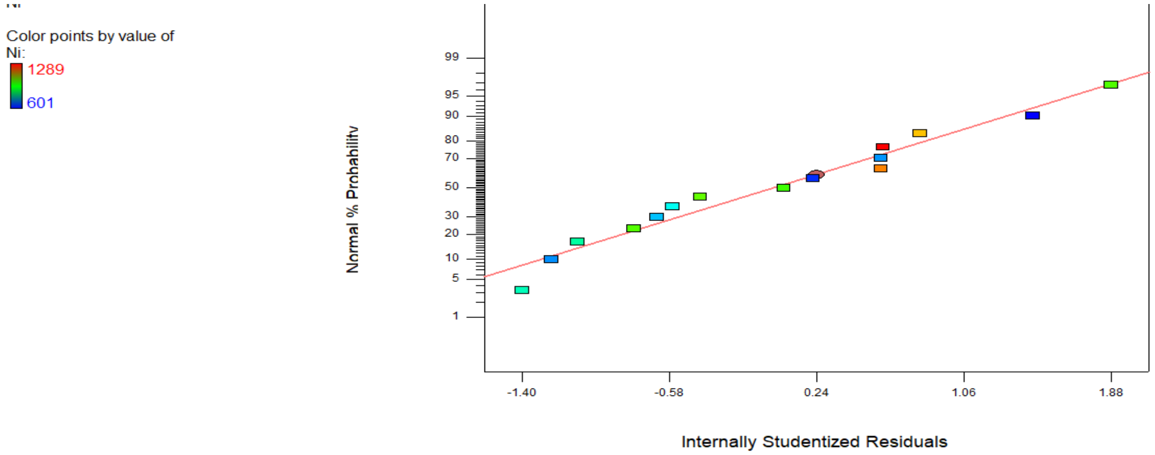


Figure E -7: Normal Plot of Residuals

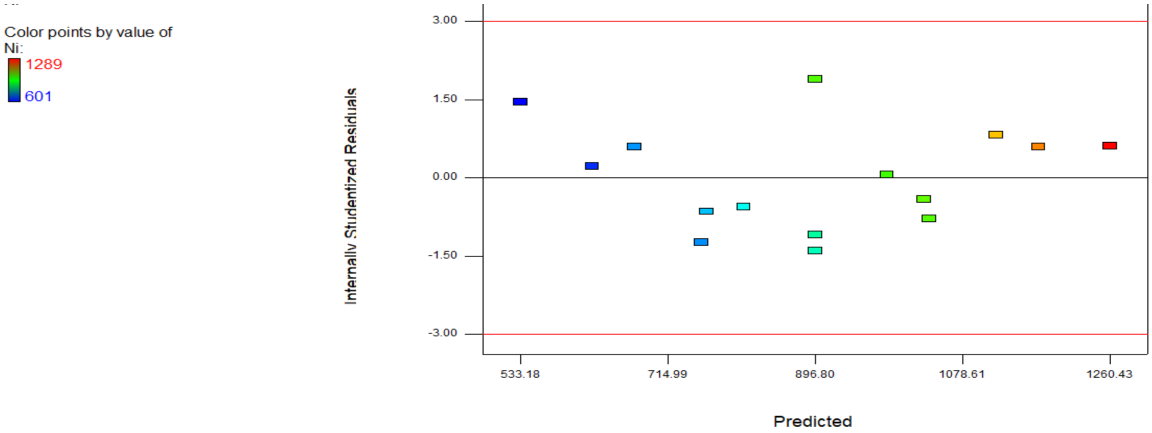


Figure E-8: Plot of Residuals Vs. Predicted Values

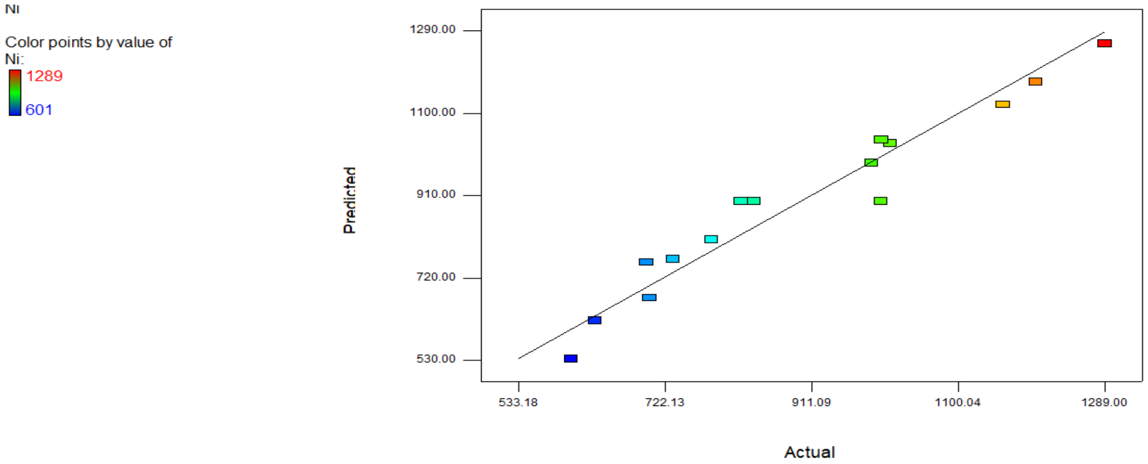


Figure E-9: Plot of Predicted Vs. Actual Values

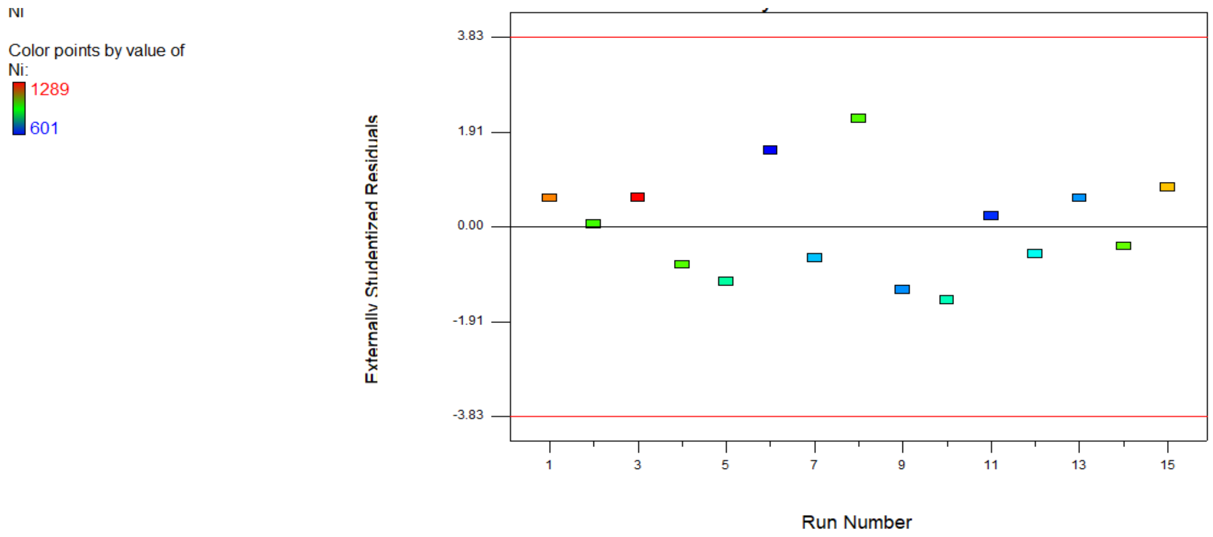


Figure E-10: Plot of Externally Studentized Residuals

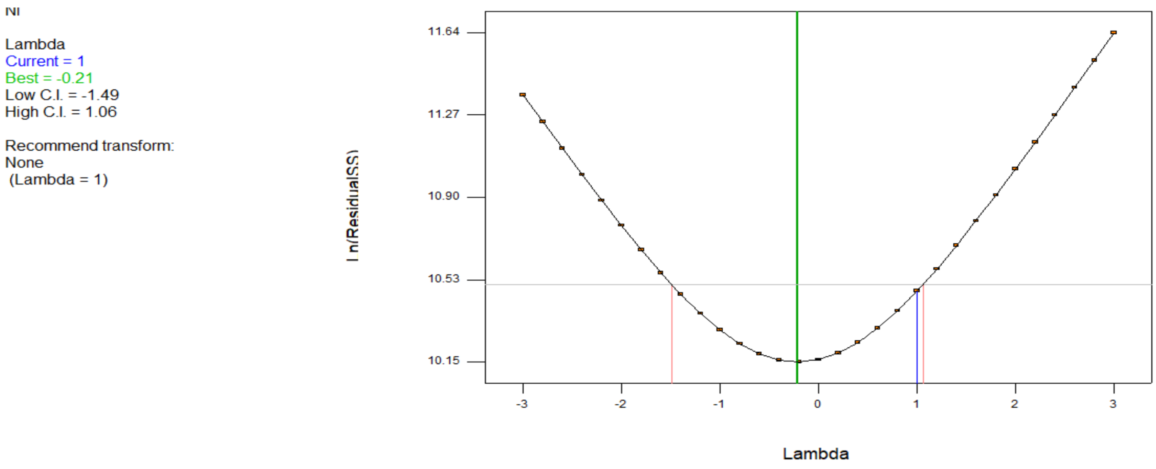


Figure E-11: Box – Cox plot For power Transforms