COMBINING PHYTOREMEDIATION WITH BIOENERGY PRODUCTION; EXPLORING OPTIONS FOR SUSTAINABLE REMEDIATION

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Declaration

I hereby declare that the contents of this thesis, except where references are formally made to the works of others within text, is the original work of the author. This thesis has not been previously submitted in whole or in part for consideration for any degree in this, or any other University. This thesis is a culmination of work done by me and does not contain any outcome of work done in collaboration unless categorically indicated in the text.

Obed Nadari Amabogha
December, 2022

Signature_________________  __________________________________

Date____________16TH DECEMBER 2022____________________________________

Abstract

Uncontrolled metal deposition in soil constitutes a serious concern for the environment due to associated risks of metal toxicity to the biota and consequently to humans. Since metals are non-biodegradable, mitigating exposure risks is reliant on either removing metals from soil, or altering their speciation in ways where their bioavailability and mobility is reduced to safer levels. The use of plants to extract metal contaminants from soil has been proposed as a cost-effective means of remediation, especially when augmented with plant growth promoting bacteria and utilizing energy crops for this process is a useful way of attaining sustainable added value from the process. The focus of this research was to examine phytoremediation as a sustainable biotechnology to remediate metal-contaminated soil, generate bioenergy and to explore the potential of using its by-products for contaminant stabilization and as adsorbents.

A multicriteria decision analysis, based on relevant criteria and key performance indicators was used to uniquely develop a mechanism for selecting plant species that satisfies the suitability criteria for both phytoremediation and biomass valorisation and silvergrass and sunflower emerged as the top performers as they incorporate important features beneficial for phytoremediation and bioenergy production. Greenhouse phytoextraction studies were carried out using sunflower plants in pots and the effect of plant growth promoting bacteria, *Bacillus aryabhattai* on growth and phytoextraction effectiveness was investigated. Sunflower plants were found to be largely effective in accumulating metal contaminants into its aboveground tissues (with bioconcentration factor and translocation factor ranging from 0.81 – 0.94), and this was enhanced significantly by the application of plant growth promoting bacteria, *Bacillus aryabhattai* (with bioconcetration and translocation factor > 1 for all metals, thus attaining hyperaccumulator status). Metal-rich post-remediation sunflower residues had calorific values ranging from 17.01 to 18.04 MJ/kg and these were converted thermochemically via pyrolysis producing an estimated 22.3 % bio-oil yield free of metal contaminants and biochars (51.6% yield) and the speciation of metals in biochar matrix was analysed. Speciation studies showed that about 73.69% - 86.04% of the metals were stably stored in the non-bioavailable F3 and F4 fractions of the biochar matrix following pyrolysis, thus significantly reducing their bioavailability and mobility. Metal-rich sunflower-derived biochar were further utilized to perform column and batch experiments to ascertain the

feasibility of further attaining practical adsorbent-based remediation from metal contaminated aqueous solution using post-remediation sunflower biochar. The metal-enriched biochar was demonstrated to be highly effective adsorbent for the removal of metal contaminants in aqueous solution (91.66 – 93.67% removal in mono-metal conditions and 81 – 88.1% removal in multi-metals condition) in the order Pb > Cd > Zn. Phytoremediation offers a less intrusive, environmentally sustainable technology option for contaminant control and when combined with energy production, it opens opportunities to attain society's economic and environmental goals in a sustainable manner. By-products attained from the process like biochars can potentially offer practical application in contaminant risk management schemes and soil improvement technologies.

Dedication

To my parents, Mr, Engoye Pamariere Amabogha and Mrs Salome Amabogha for their unwavering love and support for the duration of my life. You have both made it your life's mission to ensure we get the right education and instil in us the fear of God and the hunger for excellence in all our endeavours.

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CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND

Pollution in soils from metal contamination is considered a major global environmental issue. Though occurring naturally, the bulk of concerning contamination from metals are mostly from anthropogenic sources (Zhang et al., 2015). 'Heavy metal' has been described as a group of elements with a density higher than 4 - 5 g cm^{-3}, which includes metals and metalloids like arsenic (Duffus, 2002). Metal(loid)s as a word describes those elements exhibiting some properties of both metals and non-metals. At optimal concentrations, some of these metals/metalloids are biologically essential for plant growth and development (for example, copper, nickel, and zinc are essential micronutrients that aid mechanisms necessary for normal plant growth and yield) (Singh et al., 2017). However, exposure to pollution emissions can increase this concentration to levels where they become toxic to the environment and human health. Also, because of the non-degradable nature of these metals (Kirpichtchikova et al., 2006), they can pass through different levels of the food chain via biomagnification causing poisoning and diseases to species and consequently, humans (Ali & Khan, 2019).

With globally increasing rates of human activities, soils are continuously exposed to toxic levels of metal contamination resulting in even more threats to ecosystems, surface and groundwater, safety of food and consequently human health (Kachenko & Singh, 2006). Some of the human-influenced variety of sources through which toxic metals come into the environment are mining activities (Huang et al., 2016), fertilizer application (Duruibe et al., 2007), pesticide application (Huang et al., 2016), biosolids and manures (Hamidpour et al., 2016), atmospheric deposition and use of polluted water for irrigation (Dheri et al., 2007).

On a global scale, soil pollution has been reported in over 10 million sites, with more than 50% of this figure being as a result of metal/metalloid contamination and having an estimated global economic impact of over US $10 billion per year (He et al., 2015). Notable recorded incidences of metal contaminant consequences include the Minamata disease breakout between 1932 and 1968 (Amasawa et al., 2016), the Flint, Michigan lead-contaminated water incident in 2014 (Torrice, 2016), the Hong Kong metal-contaminated drinking water incident in 2015 (Lo, 2015), and the 2015 Mariana dam disaster in Brazil (Sá et al., 2021).

In addition to the direct toxic effect of these metals, soils already polluted with them are difficult to restore as these metals are non-degradable, therefore the clean-up process often requires extensive metal extraction and are very expensive and requires high level of technical expertise (Barcelo and Poschenrieder, 2003).

Previous and current practices of metal 'clean-ups' have involved various physical, chemical, or biological processes such as incineration, soil washing, vitrification, chemical oxidation, solidification/stabilization, electrokinetic treatment, excavation and offsite treatment etc. (Barcelo and Poschenrieder, 2003; Montpetit and Lachapelle, 2017). In addition to being costly, some of these traditional methods of remediation could be very invasive and environmentally destructive (EPA, 2008). Therefore, organizations and researchers are exploring more environmentally friendly and less invasive alternative remediation processes, generally categorized as 'green remediation' (EPA, 2008). This seeks to reduce cost as well as environmental impacts associated with traditional physicochemical remediation processes. One such green remediation option gaining increasing attention is phytoremediation.

Phytoremediation is a terminology used to describe a set of techniques involving plants as the primary agent for reducing, removing, degrading, and immobilizing environmental toxins (Peer, 2005). Phytoremediation has been proposed as an environmentally sound means of remediation especially for large areas with shallow contamination (Muske et al., 2016; Schwitzguébel, 2017). Phytoremediation is especially advantageous for the following reasons: low cost, low energy input and is less harmful than alternatives (Rheay et al., 2021). Three major subsets of phytoremediation may be identified:

- Phytoextraction which describes the removal of environmental toxins from the soil into plant tissues via translocation (Suman et al., 2018);
- Phytovolatilization which is essentially the volatilization of toxic pollutants from soil or water bodies into the atmosphere through plants (Zayed et al., 2020);
- Phytostabilization which involves the use of plants to stabilize pollutants in soil and make them less mobile and less bioavailable (Shackira & Puthur, 2019);

Ultimately, the aim of phytoremediation is to restore polluted sites to relatively safe levels of contamination (Muske et al., 2016). Simultaneously applying a combination of these different forms of phytoremediation increases the effectiveness of the process in tackling multiple kinds of contaminants at the same time (Kushwaha et al., 2015). Phytoextraction is however the area of major focus for this thesis because of its importance in removal of metals from soil.

For all its merits, phytoremediation is limited by the amount of time it takes to reach the stipulated remediation targets and in cases where it is used for metal removal, dealing with the metal-rich biomass generated by the phytoremediation process is always problematic (Lievens et al., 2008). To deem phytoremediation viable will depend a great deal on its ability to yield additional value-added services to make up for the prolonged time it takes to achieve the desired clean-up targets (Pandey et al., 2016) and the feasibility of dealing with residual metal-rich biomass derived from the process (Lievens et al., 2008).

Generating additional energy from the phytoremediation process by utilizing energy crops for metal extraction can be a useful way of gaining added value from the process. By exposing these crops to an energy valorization process, they can yield valuable energy output (Rheay et al., 2021).

The term valorization describes a process of converting biomass or waste into energy fuels and other beneficial materials (Nzihou, 2010). Biomass can be valorized via processes like combustion, gasification, and pyrolysis. Combustion is the thermal decomposition of fuel in the presence of oxygen in the air (Demirbas, 2007). Gasification involves the thermal decomposition of fuel (solid or liquid) to produce syngas (Sikarwar et al., 2016). Pyrolysis is the thermal decomposition of organic material in the absence of oxygen (Mandal et al., 2017). During pyrolysis, due to the absence of oxygen, these organic materials do not combust, but their constituent chemical compounds (cellulose, hemicellulose, and lignin) are converted to combustible gases and char. These gases can further be condensed to produce bio-oils. The pyrolysis process in summary produces three products: bio-oils, biochar and syngas (see figure 1.1). Pyrolysis is especially more environmentally beneficial because it tends to produce fewer emissions due to less oxygen usage and it produces more usable post-valorization products (bio-oil, biochar, and gases) than conventional incineration procedures (Akhtar et al., 2018).

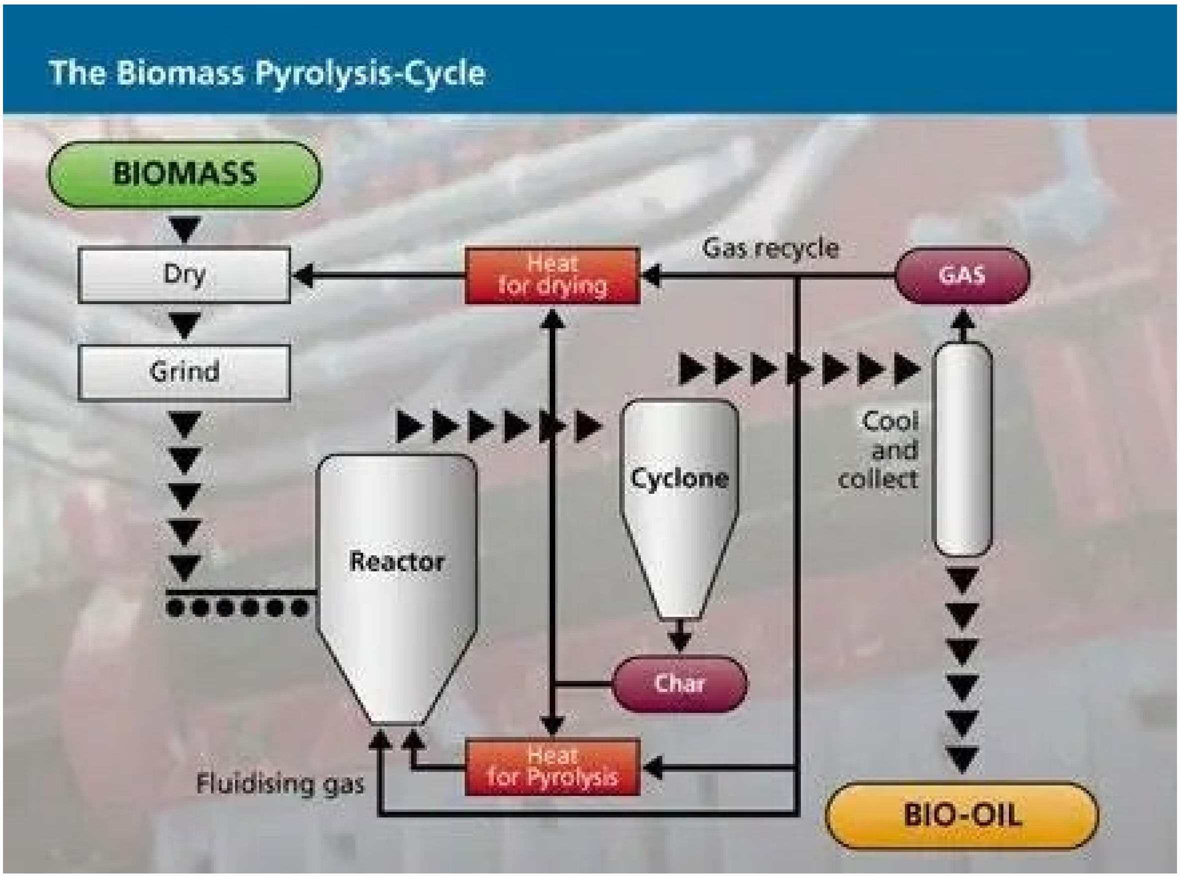


Figure 1. 1. Schematic representation of the pyrolysis process (Bioenergy Consult, 2022)

Remediation is inherently not sustainable (Bardos et al., 2020) and a common theme of many ex-situ remediation technologies is the consequent environmental degradation and the destruction of soil ecosystems and its associated functions (Scow et al., 2020). In-situ green remediation alternatives like phytoremediation are generally favoured by enlightened stakeholders (Andersson-Sköld et al., 2014; Gerhardt et al., 2017; GREENLAND, 2014), but despite it being a low-cost, effective, and relatively safe remediation technology, its acceptability is not overwhelmingly widespread (Gerhardt et al., 2017; Weir & Doty, 2016). To influence social acceptability of phytoremediation technology, key components to put into consideration are risk perception and values (Shindler et al., 2004). Emphasis has been placed on the need to adopt a more sustainable and risk management-based approach to dealing with environmental contaminants of concern (Bardos et al., 2020; Drenning et al., 2022). Low-input green remediation options like phytoremediation may be incorporated with an extensive ‘phytomanagement’ approach (which entails integrating phytoremediation with some valuable land conservation practice aimed at enabling crop production for economic and environmental gains) (GREENLAND, 2014, Cundy et al., 2016, Burges et al., 2018). To achieve these aims, generation of beneficial biomass is essential. Some successful integration of these phytomanagement practices have been successfully adopted at field scales. Quintela-Sabaris et al. (2017) using *Lactuva sativa* L. (lettuce) as a model plant investigated the effectiveness of phytomanagement using gentle remediation options on ten trace-element contaminated European soils. Results showed success in improving shoot dry weight yield of lettuce, an amelioration effect of lettuce on phytomanaged soils, even though the effect on trace element concentrations in the soil pore water was limited. Mench et al. (2018) utilizing a long-term field trial demonstrated that the simultaneous application of compost and growing of sunflower in copper (Cu) contaminated soils was successful in improving sunflower growth, soil pH, soil nutrient status of the sites, and also enhanced shoot Cu removal by the sunflower plants. Cundy et al. (2021) also demonstrated successful application of field-scale phytomanagement at a carbon tetrachloride (CCl_4)- impacted site, effectively reducing risks over the 10-year period since its implementation by removing approximately 300 – 600 g of CCl_4 annually.

There is increasing international interests in developing avenues to enhance sustainability in remediation projects. Initiatives like the EU-sponsored HOMBRE (HOlistic Measurement of Brownfield Regeneration) project was particularly focused on developing a synergistic application of brownfield regeneration with additional environmental services to promote sustainability in regeneration and remediation and a key outcome of the project was on the importance of the combination of bioenergy production and remediation as a means of generating value from marginal lands (HOMBRE, 2012). Additionally, the EU-funded GREENLAND project which is a culmination of 16 case studies including 13 long-term large-scale experiments were carried out across Europe to evaluate the effectiveness of ‘gentle remediation options’ (like phytoextraction, trace element immobilization, in situ phytoexclusion/stabilization) in managing the risks associated with trace element contamination. The project showed wide range of success stories ranging from trace element contamination reduction, improved trace element tolerance, dry biomass yield enhancement, soil improvement, reduced metal mobility across contaminated sites in Europe

(GREENLAND, 2014). The end goal is to seek low-input mechanisms to improve sustainability in risk management-based green remediation.

According to the United Nations Brundtland report in 1987, sustainability is defined as *"meeting the needs of the present without compromising the ability of future generations to meet their own needs"* (WCED & Brundtland, 1987). It entails attaining society's economic and social needs together with protecting the environment. The Sustainable Remediation Forum in the UK (SuRF) defined sustainable remediation as *"a remedy or combination of remedies whose net benefit on human health and the environment is maximized through judicious use of limited resources"* (SURF, 2009). The forum already developed a framework to support land conservation decision-making in a manner that merges well with prevalent good environmental practice guidance for contaminant risk assessment and management (Bardos et al., 2012). Tiered approach to sustainability is advocated for gentle remediation options with assessment tiers ranging from simple qualitative assessment to multicriteria decision analysis and monetized cost-benefit analysis (SuRF, 2009). The Sustainable remediation initiative also prioritizes assessment and reduction of the potential impact of every dimension of the triple bottom line: environment, economy, and society (SuRF, 2009). This study seeks to merge these priorities together via phytoextraction of heavy metal contaminants from polluted soils and gaining valuable bioenergy proceeds from the process.

In compliance to sustainable remediation provisions, the GREENLAND project also demonstrated that biomass generated from gentle remediation practices can be valorized via some mechanisms like combustion, anaerobic digestion and pyrolysis thereby proving renewable low-input energy (GREENLAND, 2014). Although the concept of combining phytoremediation with biomass valorization is relatively new, quite a number of works has been done on the subject. In a review using four bioenergy crops as case study, Pandey et al. (2016) explored potential strategies for linking phytoremediation and bioenergy production. Their report and a number of other studies (Jiang et al., 2015; Tripathi et al., 2016) have evaluated specific bioenergy crops (based on hyperaccumulation and biofuel potentials) as candidates for a synergistic association with phytoremediation. However, none of these studies has carried out an across board analytical review, involving multiple species as well as considering multiple suitability criteria to determine suitable candidates for a synergistic approach to pollution clean-ups. Developing a more robust selection process would vastly improve understanding. Also, the expected outcome is realistically more reliable as candidates have been exposed to more suitability checks.

To generate energy from phytoremediation-derived solid biomass, sometimes metal-rich biomass is subject to direct combustion to generate heat that can be transformed to electric power (Kshirsagar & Kalamkar, 2014). However, certain metals like zinc and cadmium have huge volatilization potential when combusted under extreme temperatures and could yield concentrated heavy metals in the volatile fractions (Lievens et al., 2008). A thermal conversion process like pyrolysis is therefore desirable to reduce the volume of metal contaminants in the volatile fractions so it can be utilized for chemicals or transportation fuels (Lievens et al., 2008). Under pyrolysis, the metal mass can be stably stored in the solid carbon rich biochars fraction, leaving the oil, tar, and gas fractions free of heavy metals (Chalot et al., 2012; Lievens et al., 2008). This stabilized metal-rich biochar can potentially be disposed safely or even further explored as a contaminant removal material. Even though biochar is known for its use as soil amendments (Inyang et al., 2012) and wastewater treatment materials (Manyuchi et al., 2018), their applicability as treatment materials when enriched with bulk volumes of metals (after pyrolysis) have not been adequately tested and knowledge of their ecotoxicity when disposed into the environment is very limited. To avoid further exposure to heavy metal contamination after clean-up, it is expedient to evaluate the toxicity of biochar enriched with metals and evaluate their suitability as wastewater treatment materials. Their potential use for wastewater treatment provides further options for additional benefits from the process.

1.2 JUSTIFICATION OF STUDY AND CONTRIBUTION TO KNOWLEDGE

It has been argued that the commercial success of phytoremediation as a pollutant control technique is dependent on its potential to generate valuable biomass as by-products (Lelie et al., 2001; Conesa et al., 2012). As a stand-alone remediation technique, it may be less favourable than alternative means for reasons stated in section 1.1. The potential reuse of its post-remediation biomass is hugely what makes the process environmentally appealing. Biomass refers to any fuel derived from organic materials (Dastyar et al., 2019). They are renewable and can be obtained with relative ease. Some viable biomass identified as useful for valorization and energy generation are scrap lumber, waste residue feedstock, timber debris, manure, and crop residue.

A major challenge of using phytoremediation feedstock for valorisation and bioenergy generation is pollutant transfer and the presence of metal contaminant in usable biomass after phytoextraction. Additionally, plants ideal for phytoremediation are expected to have additional beneficial traits to be useful. This is further compounded by plants needing to satisfy bioenergy and valorisation requirements as well. This presents a unique problem and is identified as a major weakness of the technology (Gomes, 2012).

This research presents a comprehensive and cohesive approach to solving these problems. It utilizes a unique cradle-to-the-grave approach to exploring phytoremediation as a sustainable and beneficial means of managing metal pollution. Firstly, the study utilizes an MCDA to uniquely develop a mechanism for selecting plant species that satisfies the suitability criteria for both phytoremediation and biomass valorisation, then utilizes the information gathered to conduct an empirical phytoremediation study whose by-products will then feed into a valorisation study (pyrolysis). By-products (biochar) from this process will then be used to perform column and batch experiments to demonstrate their effectiveness as surfaces for wastewater treatments.

While individual sections of these different processes have been done in different ways in isolation, none has carried out a cohesive synergistic approach by merging these processes where derived outcomes of one process are fed into the next. It presents a unique pathway for developing solutions to environmental problems in multiple strands that considers both environmental and economic concerns from the onset as well as present a way of managing wastes and transfer of contamination by encouraging reuse of by-products.

1.3 RESEARCH GAPS AND PROJECT AIM AND OBJECTIVES

From the literature review (see Chapter 2), the identified research gaps that require further investigation are outlined thus:

i. SuRF-UK advocates a tiered perspective to assessing sustainability and stresses the need for decision making efforts to be proportionate, i.e., aiming to make decisions based on the simplest approach that demonstrably produces the most optimum and robust outcome (Bardos et al., 2012). Most phytoremediation projects with bioenergy crop considerations generally involve an evaluation of specific bioenergy crops of interest based on phytoextraction and biofuel potential. There is a lack of a systematic data-based selection review process involving multiple candidates and considering multiple suitability criteria when decisions are being made on plants to be adopted for a synergistic approach to metal contamination clean-up.

ii. Improving the biomass productivity and ultimately the accumulation potential of plants is key for any phytoremediation project. *Bacillus aryabhattai* has been identified and demonstrated as a plant growth promoting bacteria (Bhattacharyya et al., 2017). Because of its genome-level observation as a plant growth promoter, the potential exists that it could even be more beneficial in aiding plant to maximise and improve their metal accumulation capacity and boost their tolerance to metal stress. It will be the first time *B. aryabhattai* will be evaluated for its potential to enhance phytoremediation.

iii. While there are studies exploring the competitive sorption of heavy metal using different types of sorbents, very few of these studies have explored competitive sorption dynamics using biochar and there have been no report of the use of metal-rich biochar from sunflower derived from a phytoremediation process as an adsorbent in aqueous settings.

iv. In addition to other individual identified gaps, there has been no cohesive cradle-to-the grave exploration of the sustainability of phytoremediation from the selection of the ideal species to the use and reuse of products and by-products, down to the potential disposal of end-products of the process.

The cradle-to-the-grave approach is a life-cycle assessment tool typically used to explore the associated impacts at each stage of a product's life cycle (EEA, 2022). For the context of this study, the research aims to use the cradle-to-the-grave approach in multi-stages to comprehensively examine phytoremediation as a sustainable biotechnology to remediate metal-contaminated soil, generate bioenergy and to explore the potential of using its by-products for contaminant stabilization and as adsorbents for wastewater treatment (See Figure 1.2).

To achieve this aim, the study would be conducted based on these set objectives:

- To develop a multi-criteria analysis matrix based on a number of established criteria to determine which phytoremediation species is (are) best suited for the purpose of phytoremediation and bioenergy generation.
- To ascertain the effectiveness of select phytoremediation species in clean-up of metal pollution on metal contaminated soils as well as investigate the effect of plant growth promoting bacteria (PGPB), *Bacillus aryabhattai* in improving plants' heavy metal bioaccumulation potential.
- To evaluate the bioenergy potential of the post-phytoremediation biomass, and the production of biochar
- To evaluate the potential use of post-pyrolysis metal-rich biochar for wastewater treatments of heavy metal contaminants of concern.

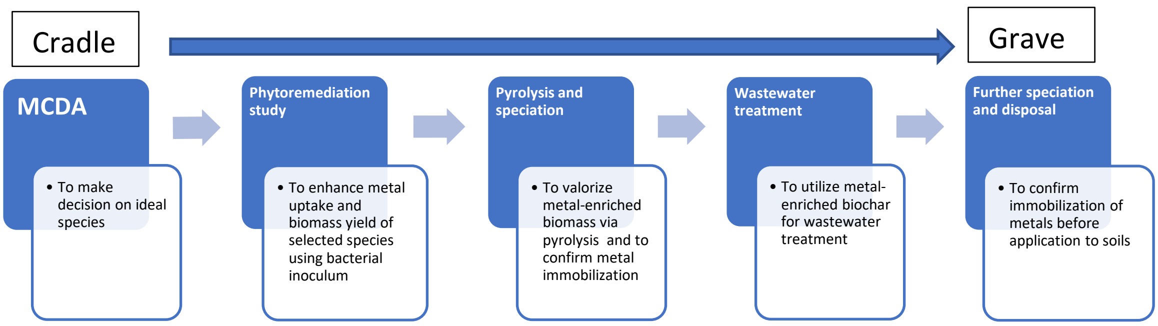


Figure 1.2. Flow diagram showing cradle-to-the-grave approach highlighting objectives

1.4 THESIS OUTLINE

The thesis consists of 7 chapters outline as follows:

Chapter 1 introduces the research topic and highlights the identified knowledge gaps while outlining the research aims and objectives and proposed thesis structure.

Chapter 2 gives a comprehensive review of relevant literature relating to the associated subjects around the research. It discusses the conceptual framework underpinning the important research themes such as metal pollution, phytoremediation, biomass valorization, bioenergy generation and explores the applicability of biochars as materials for wastewater treatment.

Chapter 3 reviews the methodological approach employed, their designs and rationale for use as well as materials, technique and equipment employed.

Chapter 4 **i**ntroduces the concept of multicriteria decision analysis, the resulting MCDA matrix, a result section highlighting findings and a section detailing with the application ramifications and summary. The results garnered from this chapter informed the choice of plant species to be employed for the next chapter.

Chapter 5 gives a brief introduction section detailing the rationale behind the study, reports on a preliminary study investigating the usefulness of a plant material *(Helianthus annuus),* in accumulating metal contaminants onto its aboveground tissues, and investigates the effect of PGPB, *Bacillus aryabhattai* on improving the growth and bioaccumulation potential of *H. anuus.*

Chapter 6 includes an introduction section summarizing the findings of the phytoextraction process, details the findings of the pyrolysis study and analysis of the constituent products, especially the biochar obtained and investigated using column experiments, the adsorption potential of metal-rich sunflower biochar to clean-up rare-earth metal pollution in aqueous solutions.

Chapter 7 gives a general discussion of the research as a unit, concludes the thesis and considers the implications of all the findings, their significance, the limitations, and highlights recommendations for future research.

1.5 Significance of the study

The findings from this study have potential wider positive implications in several ways:

- Remediation of metal-contaminated sites remains a layered and complex issue. As will be illustrated in this study, remediation occurs in multiple strands of processes and a better understanding of species performance dynamics across the different stages will save time, minimize costs, provide important information on possible hazards associated with contaminants' mobility and toxicity, and presents workable and sustainable management options to the problems of metal contamination.
- Results obtained from this research will provide data-based information to academia, industries, and the public on sustainable phytoremediation technology using energy crops and options to deal with its associated by-products, as well as identify areas necessary for further studies and exploration.
- The study will contribute to the already rich evidence on the behaviour of heavy metals in the environment and the potential associated risks to life forms and human health.

CHAPTER TWO

LITERATURE REVIEW

2.1 Soil contamination

Soils are a hub of some of world's most important biodiversity (Delgado-Baquerizo et al., 2020). They are the core provider of water and nutrients essential for plant life and other associated organisms (Delgado-Baquerizo et al., 2020).

In recent times however, these soils are continuously burdened with degradation and pollution from human activities, consequently reducing their capacity to provide essential ecosystem services and making the soils and their accompanying run-off water harmful to the environment and humans (UNEP, 2021). These sorts of harmful soil degradation are chiefly caused by the increasing presence of xenobiotic chemicals in the natural environment.

Chemical contaminants in soils with potential to cause harm to human health and the environment can be organic or inorganic compounds.

Organic contaminants are generally described as carbon-based molecules that are toxic, persistent and have huge potential to cause harm to the environment and humans. They are to a large extent of man-made origin, but these compounds can also be a product of natural processes like volcanic eruptions and wildfires. Organic contaminants can be a product of emissions from some unintentional industrial processes like mining that releases polycyclic aromatic hydrocarbons (PAHs), or they could be synthetically made for specific human uses as in the case of pesticides, industrial chemicals, and intermediate chemicals (e.g., polychlorinated biphenyls (PCBs)) (FAO & UNEP, 2021). Some examples of organic contaminants are chloroform, polyfluorinated chemicals (PFCs), dichloro-diphenyl-trichloroethane (DDT), polybrominated diphenyl ethers (PBDEs), ethane, benzene, toluene, ethyl benzene, xylene, PAHs, and PCBs.

Inorganic contaminants are a group of basically non-carbon elements and compounds that either occur naturally in parent rock or originates from human activities (FAO & UNEP, 2021). Three main class of inorganic contaminants are radionuclides, asbestos, and trace elements.

- Radionuclide contaminants produce ionising radiation as active atoms decay therefore presenting potential risks for organisms and the environment.
- The term asbestos describes a group of naturally occurring, heat-resistant and hydrated mineral silicate fibres belonging to the serpentine and amphibole groups of rock-forming minerals (FAO & UNEP, 2021). These mineral silicates were widely used for making different forms of building materials and are known to be harmful to human health.
- Trace elements are a group of common elements that exists normally at low concentrations in the environment and poses high toxicity risks to living organisms (FAO & UNEP, 2021). They include non-metals such as antimony (Sb), selenium (Se) and arsenic (As) as well as 'heavy metals' such as lead (Pb), zinc (Zn), cadmium (Cd), cobalt (Co), chromium (Cr), mercury (Hg), copper (Cu), tin (Sn) and nickel (Ni). These elements are very persistent in the environment and cannot be degraded by regular metabolic processes.

2.2 Heavy metals contamination

Metals associated with environmental toxicity are usually described by a generic term 'heavy metals.' There is no universally established definition of the term 'heavy metal' by a globally renowned authority, not even by the world's authority on chemical nomenclature and terminology, International Union for Pure and Applied Chemistry (IUPAC). In over seven decades of its use in Chemistry, it has been defined in terms of elemental densities (Bjerrum, 1936; McNaught, 1997), atomic mass (Lewis, 1993, Rand et al., 1995), atomic number (Venugopal and Luckey, 1975; Hale and Margham, 1988) and other chemical properties (Hampel and Hawley, 1976; Bates and Jackson 1987; Wyman & Stevenson, 1991). However, none of these physicochemical concepts has any relationship with toxicity. Even though the use of this term is persistently rising in literature, there is no clear chemical basis for its continuous use and although the term has been used consistently in the context of toxicity, there is no inherent connection between 'toxicity' and 'heaviness.' However, a lot of these 'heavy metals' are known for their toxicity at certain concentrations. Duffus (2002) argued that the term be abandoned because of lack of correlation between density (heaviness) to any physicochemical features with which heavy metals has been described with. He further opined that metal classification should be strictly based on their chemical properties and nothing else.

The use of the term ‘heavy metal’ in environmental literature is still very widespread and increasing. A complete abandonment or a replacement of the term may appear non-intuitive to scientists in the field as it is widely established in environmental publications and scientists generally understand the contextual meaning behind its use. It is also important that its definition is clear and have some scientific credence. For simplicity and consistency, Ali & Khan (2018) opined that an acceptable definition needs to be based on the periodic table of elements (a chemical property), at the same time satisfy its property of heaviness (density). Since elements placement on the periodic table are based on their atomic number and density describes *heaviness,* they defined heavy metals as *naturally occurring metals with elemental density above 5 g* cm^{-3} *and atomic number above 20*. Based on this definition offered, the periodic table yielded about 51 elements categorized as heavy metals. Examples include Cr, Zn, Pb etc. This report will be adopting the definition of heavy metals offered by Ali & Khan, 2018.

Heavy metals are introduced to the environment via natural, agricultural, industrial, and atmospheric sources as well as domestic effluents. Harmful human activities have contaminated locations in the world with elements such as Cd, Cr, Cu, Pb, Ni, Zn in Australia (Smith et al., 1996), Pb, Cd and Cu in Albania (Shallari et al., 1998), Cd, Zn and Cu in China, Japan, and Indonesia (Herawati et al., 2000), Hg, Pb, Cd, Cr, Ni, Tl in Kenya (Kinuthia et al., 2020) and As, Cd, Cr amongst others in Peru (Piñeiro et al., 2021). These metals pose great risk to the environment, human health and the other organisms by their release and concentration in the food chain (Bat et al., 2012). Particulate matter can be ingested by organisms and transferred to humans causing serious health hazards. These metals can still be transferred via runoff into water courses causing serious contamination to aquatic life and drinking water supply channels.

2.3 Heavy metal classification

As will be detailed in section 3.2 of chapter 3, heavy metal of concern referred to in this study are Cd, Cr, Cu, Ni, Pb, and Zn. They are among the commonest metals investigated in literature, known for their persistence, and pronounced threat on human health and the environment (Aziz et al., 2008; Covelo et al., 2007; Osma et al., 2013).

- **Cadmium (Cd):**

Cadmium is considered 7th in ATSDR substance priority list (ATSDR, 2019). It is a metal that is very widely distributed across the earth's crust with an average concentration of 0.1mg/kg. It was first used as a tin substitute in World War I and as a pigment in paint industries and it is currently being used for special alloy production in rechargeable batteries and is also a constituent in tobacco smoke (Jaishankar et al., 2014).

Exposure to humans is primarily by ingestion and inhalation and has huge potential to result in acute intoxications. The Agency for Toxic Substance and Disease Registry estimated the number of workers exposed to cadmium toxicity in the US at 500,000 per year (Mutlu et al., 2012). Due to its depositions in soils via food chains and its high rate of soil to plant transfer, cadmium is predominantly found in fruits and vegetables (Satarug, 2011). Exposure to these food substances increases risks to associated human health hazards. An important source of Cadmium contamination of soils is via the use of commercial fertilizers derived from rock phosphates (Ulridge, 2019) as well as from sewage sludge (Din et al., 2021) directly linking its environmental ubiquity to human activities. Cadmium is primarily a pulmonary, renal, and gastrointestinal irritant that can cause a range of clinical effects ranging from emphysema, aminoaciduria to glucosuria and proteinuria (Mahurpawa, 2015).

When absorbed and accumulated by plants above known threshold for plants (32 mg/kg dry weight in soil), cadmium stress can lead to a marked decline in its rate of photosynthesis and consequently a negative effect on biomass production; also disrupts plants oxidative processes and can lead to nutrient uptake imbalance (EPA, 2007; Zou et al., 2017). The bioavailability of Cd however can be influenced by a system's pH and as such phytotoxicity thresholds can differ under some contaminated land regimes depending on soil pH (Soubasakou et al., 2022). Increased soil acidity correlates with higher conversion of soil Cd to forms that are more available to plants, hence increasing its phytotoxicity (Mondal et al., 2020).

- **Chromium (Cr):**

Chromium is the 7th most abundant element on the earth crust (Mohanty & Kumar, 2013). Chromium exists in a range of oxidative states from Cr(II) to Cr(VI) with Cr(III) and Cr(VI) being its most common. Natural source of chromium pollution is primarily via leaching from rocks and topsoil, polluting groundwater (Jaishankar et al., 2014; Hausladen et al., 2018). Anthropogenic sources are mainly via burning of coal and oil, drilling of oil wells, pigment oxidants, metal plating tanneries, chromium steel sewages and fertilizers, (Ghani, 2011; Jaishankar et al., 2014).

Exposure to humans comes in the form of industrial dusts/fumes as well as via polluted food. It attacks mostly the pulmonary organs and can cause ulcer, respiratory cancer and can also perforate the nasal septum (Mahurpawa, 2015). Cr(VI) is considered one which pose the most carcinogenic risk (Chen et al., 2019).

In plants, exposure to Cr(III, VI) can lead to inhibition in seed germination, seedling development, root growth and consequently biomass production. Its presence in plants can also induce leaf chlorosis and necrosis (Singh et al., 2013). No known phytotoxicity thresholds have been established for Cr(III, VI) (EPA, 2007). However, its toxicity is strongly determined by its speciation and Cr(VI) is considered more environmentally mobile than Cr(III) (Botsou et al., 2022). Even though no phytotoxicity threshold has been established for Cr, higher environmental mobility of Cr(VI) suggest they are more bioavailable for plants than Cr(III) and therefore potentially more toxic (Botsou et al., 2022).

- **Copper (Cu):**

Copper is regarded widely as one of the most essential elements for plant, animal and human growth and development. It is very abundant in the environment with the NMIC, 2016 estimating its global annual production in 2015 at 18.7 million metric tons and this figure is still rising. Some natural sources of copper are decaying vegetation, forest fires, wind-blown dusts, and sea spray while major anthropogenic sources are through mining, phosphate fertilizer production and metal production.

At concentrations above stipulated toxicity thresholds (70 mg/kg dry weight in soil), copper can be very toxic (EPA, 2007). Entry to the human body is mainly via ingestion from food/water and from dust/fumes. Copper can cause irritations to the sensory organs causing dizziness, headaches, vomiting and diarrhoea (ATSDR, 2004).

Its toxic effect on plants is primarily towards root growth and morphology because of its tendency to accumulate at the root with little translocation upwards towards the shoot (Marschner, 1995). Its effects on the root are reflected in disruption of root cuticle formation and reduction in root hair proliferation.

- **Lead (Pb):**

Lead is a toxic metal of great global concern whose use has caused extensive contamination in parts of the world. Sources of lead in the environment are metal plating and finishing, smelting of ores, soil wastes, factory chimneys, gasoline and pigment additives, fertilizers/ pesticides, and automobile exhausts. Plants take up some of these lead to fix in soils and these can be washed into water bodies via runoff thereby increasing human exposure to associated risks. Exposure to humans is primarily via food/water and fumes (Goyer, 1990). Lead primarily attacks the renal, hematopoietic, and nervous systems. Long-term exposure could lead to clinical effects such as anaemia, central nervous disorders, encephalopathy, and peripheral neuropathy (Mahurpawa, 2015).

Unlike some beneficial metals such as zinc and manganese, lead offers no beneficial biological function to plant growth or development. When above phytotoxicity threshold (120 mg/kg dry weight in soil), It disrupts several physiological processes essential for plant growth and survival (EPA, 2007). Lead poisoning have been shown to cause damage in chlorophyll and photosynthetic processes (Najeeb et al., 2017), debasing plant quality (Yongsheng et al., 2011), instability and plant ion uptake (Jaishankar et al., 2014).

- **Nickel (Ni):**

Nickel is a ubiquitous transition metal distributed extensively across the environment, soil, water, and air. It occurs in several oxidative states ranging from -1 to +4 with oxidative state +2 (Ni^{2+}) being the most common in biological systems and the environment (Muñoz & Costa, 2012). Due to the uniqueness in its chemical and physical properties, nickel can be used in modern metallurgy for processes like electroplating, battery production, alloy production and they can serve as catalysts in food and chemical industries. Like most metals, nickel has both natural and anthropogenic sources.

The health effects of nickel on human health can vary depends on the quantity and duration of exposure. Some clinical effects recognized are respiratory tract cancer, asthma, contact dermatitis and lung fibrosis (Chen et al., 2017).

At concentrations above its phytotoxicity threshold (38 mg/kg dry weight in soil), plant exposure to nickel can cause stunted shoot and root growth, deformation in various plant parts, biomass production reduction, and chlorosis and necrosis (EPA, 2007; Ahmad & Ashraf, 2012).

- **Zinc (Zn)**

Zinc is one of the most important trace elements necessary for the growth of plants, animals, and microorganisms. It is also present in high concentrations in human body tissues and secretions with the average amount in a mature adult at 1.4 - 2.3 g (Bhowmik et al., 2010). Zinc is also important to human diet via the role it plays as a structural constituent in a number of enzymes necessary for energy metabolism (Alloway, 1995). However, when concentrations exceed certain toxicity threshold and for the long-term, zinc can pose some serious health risks such as pancreatic damage, anaemia, reduction in levels of high-density lipoprotein cholesterol (Hooper et al., 1980).

Zinc sources are majorly through products from industrial processes such as smelter waste discharges, coal and fly ash, wood preservatives, fertilizers, and mine tailings.
Even though zinc is generally beneficial to plants, above certified concentration thresholds (160 mg/kg dry weight in soil) they can be toxic to plants (EPA, 2007). Zinc has been shown to

cause disruption in the cortical cells of plants, cell organelles disintegration and a structureless cytoplasm (Rout & Das, 2009).

2.4 Remediation

The optimal remediation process functions to manage risks associated with environmental pollution or contamination in environmental media like soil, water (ground or surface) and sediments (Drenning et al., 2022). It seeks to mitigate potential effects of contaminants to human health and the environment. For metal contaminants, the remediation process may be conducted in-situ or ex-situ and can be based on several mechanisms such as physical, electrochemical, thermal, chemical, and biological remediation.

2.4.1 Physical remediation

2.4.1.1 Soil replacement

This involves wholly or partly replacing contaminated soil with non-contaminated ones. In this process, contaminated soils are excavated and disposed offsite and cleaner ones are placed on site. This was the most used remediation practice prior to 1984 before the emergence and popularization of newer alternatives (Khalid et al., 2017). The replaced soil could either be treated to remove contamination or dumped in some marginal site or landfill. Soil replacement essentially seeks to dilute heavy metal-contaminated soil with newer soils to sustain and increase soil functionality (Yao et al. 2012) and it has been shown by Douay et al. (2008) to be a successful technique as replacement of soils in a Pb and Cd contaminated site in north of France resulted in a successful revegetation of land with cultivated crops which also led to increase in soil quality. This method is however highly labour and capital intensive and is mostly utilized for very contaminated soils that covers a relatively small area. The cost for excavation and transportation of contaminated soils offsite over a short distance is estimated at $270 to $460 per ton and could be significantly higher with longer distance transportation (Khalid et al., 2017).

2.4.1.2 Soil isolation

Soil isolation process involves separating metal-contaminated soils with noncontaminated ones, often used alongside complimentary auxiliary engineering measures for complete remediation (Zheng & Whang, 2002). The process looks to restrict contaminants within a specific area thereby preventing metal contaminant movement off-site (Zhu et al., 2012). For example, this could be achieved by using subsurface barriers to restrict flow of contaminated surface/ground water at a polluted site. The lateral flow of contaminated groundwater can be restricted by using vertical subsurface barriers (Khalid et al., 2017). Materials used for subsurface barriers include grout curtains, sheet piles and slurry walls.

2.4.2 Thermal remediation

2.4.2.1 Vitrification

Vitrification means application of high temperature treatment to metal-contaminated sites to reduce the mobility of heavy metals inside soils therefore causing the formation of vitreous materials (Mallampati et al., 2015). During this process however, some metals like mercury (Hg) can be prone to volatilization and so should be collected for an alternative means of disposal or treatment. During the in-situ process of vitrification, vertically inserted electrodes passes electric current into the contaminated area of interest. Dry soils however may not be ideal for a vitrification process as there may not be enough conductance to aid the process. A recent in-field demonstration was carried out by Dellisante (2016). They reported that a Zn and Pb-rich ceramic waste land was vitrified by applying a temperature of 1850°C and this was shown to be efficient in cleaning up metal contaminants in site and can be applied on large volumes of soils. A major limitation of this process is that some soils may not meet the conditions necessary to adequately conduct electricity.

2.4.3 Electrochemical remediation

2.4.3.1 Electrokinetic remediation

A newer physical remediation process is the electrokinetic remediation which is another process involving electric current. Direct current is applied on soil to separate heavy metals in the soil via processes like electrophoresis, electric seepage, or electro-migration (Yao et al., 2012). Its operation is based on the principle that adequate electric field gradient is created on two sides of the electrolytic tank harbouring saturated inorganic pollutants (Khalid et al., 2017). This remediation method was recently shown to reduce about 60% of Hg from a contaminated soil sample of 400kg in about 3 months (Rosestolato et al., 2015). The main drawback of this remediation technique is the issue of fluctuating soil pH as this process cannot maintain stable soil pH value. Buffer solutions may need to be added to the cathode and anode using ion exchange membrane or complexant to be able to control pH values (Wang et al., 2007).

2.4.4 Chemical remediation

2.4.4.1 Soil washing

The removal of metal contaminants from soils via leaching using various extractants and reagents is referred to as soil washing (Guo et al., 2016; Park & Son, 2017). In this process, polluted soil is dug out and mixed with the ideal extractant solution suitable for the heavy metal in question. This will then be mixed thoroughly for a prescribed period and processes such as precipitation, ion exchange and adsorption will aid the separation of the soils from the contaminated leachate. The now cleaner soil can then be backfilled into its site of origin after satisfying required regulatory standard. Soil washing is a relatively rapid process and tend to completely remove all the heavy metals from contaminated soils (Park & Son, 2017). The success and effectiveness of this technique is highly dependent on the ability of the extractant solution to dissolve heavy metal of concern in soil and this must be investigated thoroughly before the process is carried out. Synthetic chelates are widely regarded as the most effective extractants for this process because of their ability to set up stabilized complexes with a lot of heavy metals in wide ranges of pH (Saifullah et al., 2015).

2.4.4.2 Immobilization

Immobilization seeks to reduce the mobility and bioavailability of heavy metals in soil via the use of specified immobilizing agents. Immobilization of heavy metals can be achieved via processes such as adsorption, precipitation, and complexation reactions. By these processes, heavy metals can be redistributed from soil solution into solid particles and as result inhibiting their mobility and bioavailability in soils. Organic and inorganic amendments are the generally common materials used as soil immobilizing agents (Ashraf et al., 2017; Shahid et al., 2014). In recent times, biomaterials have been used as agents of heavy metal immobilization because they are readily available at relatively low cost. Biochar for example have been receiving increasing attention as use for immobilization of heavy metals. They are carbon-rich porous charcoal formed as the solid fraction product of a pyrolysis process involving organic residues like wood, municipal waste, biosolids and crop residues. Studies have shown that the application of biochars to soil greatly increased heavy metal sorption abilities and reducing their mobility and bioavailability in soil (Al-Wabel et al., 2015; Puga et al., 2015; Yuan et al., 2021). Biochars alter soil's physical, chemical, and biological properties in ways that could affect their sorption behaviour. For example, it could increase soil pH which could aid precipitation and therefore affect heavy metal immobilization.

2.4.4.3 Encapsulation

This is also an immobilizing technique, but it is achieved by encapsulating the toxic metals in manageable blocks for safe disposal in landfill sites. Toxic metals can be bound by encapsulation in cement, lime or asphalt rendering them immobile and stops its spread to other materials. Cements are usually the preferred binding material because of its availability, versatility, and relative cost-effectiveness. Ordinary Portland Cement is a known metal retainer effective in stabilizing heavy metals in soils (Li et al., 2019). Another alternative established to be effective are Calcium aluminate cement (Navarro et al., 2013). Encapsulation by cement, lime and asphalt can be used simultaneously with immobilizing agents like polyvinylalcohol, agar and polyurethanes. The major limiting factor of this technique is the lack of readily available market for the solid block products resulting from the process (Mulligan et al., 2001).

2.4.5 Biological remediation

Biological remediation entails utilizing green remediation options as a solution for the problem of environmental degradation. It is defined as the use of microorganisms or plants for the removal or detoxification of organic and inorganic contaminants from the environment. It is a believed to be a relatively cost-effective clean-up option and this solution is deemed permanent because these biological agents tend to mineralize contaminants in the environment (Abioye, 2011). Biological remediation broadly makes use of microorganisms or plants (phytoremediation) as agents for removal or detoxification.

2.4.5.1 Microbial bioremediation

This type of remediation employs the use of micro-biological agents (e.g., fungi, bacteria, microalgae) to clean up contaminated land or water bodies (Strong & Burgess, 2008). It involves conditioning or stimulating microorganisms in ways where they can be able to effectively degrade hazardous pollutants to levels where they are considered safe for the environment. The general concept is to bio-transform an already altered environment to its original state via series of biological processes. It seeks to take advantage of microorganisms' ability to survive very polluted habitats via a series of mechanisms such as biosorption, bioaccumulation and biomineralization.

Biosorption is a metabolically passive process that involves utilizing biological materials as sorbents for heavy metals via physicochemical or metabolically mediated uptake pathways. It differs from bioaccumulation because bioaccumulation is a metabolically active process and requires respiration as well as energy released from the living organism accumulating the contaminant (Chojnacka, 2010).

The biomineralization concept revolves around microorganisms' ability to alter the mobility and speciation of metals, including their mineral formation or dissolution (Gadd & Pan, 2016). Microorganisms are ubiquitous naturally occurring living organism found in the environment. They are natural helpers in decomposing, recycling, and correcting alterations to conditions in soils and water bodies and if its potential is adequately amplified, they can be one of the most efficient ways to reverse some of the contaminations caused by environmentally hazardous human activities.

2.4.5.2 Phytoremediation

This refers to any form of technology that makes use of plants to remediate contaminated environmental bodies. Even though the concept of phytoremediation was first introduced in 1983 (Chaney, 1983), it has been in practice for the past 300 years. It is a practice that is considered very environmentally friendly, energy efficient, aesthetically pleasing, non-invasive and cost-effective for remediating low-to-medium levels of metal contamination (Sabir et al., 2015). As a technology, phytoremediation can be used in isolation as well as in combination with other traditional techniques of remediating contaminated sites. Its efficiency however is dependent on several plant and soil factors such as bioavailability of metals in soil, soil physicochemical properties, plant, and microbial exudates as well as plant's ability to uptake, translocate, accumulate, sequester, and detoxify harmful metals (Peer, 2005). Phytoremediation is a general term used to describe markedly different mechanisms of plant action in relation to immobilization, degradation, and removal of metal contaminants from soils (Kushwaha et al., 2015). Phytoremediation is further categorized into three (3) subdivisions based on the mechanism of plant activity. They are phytostabilization, phytovolatilization and phytoextraction.

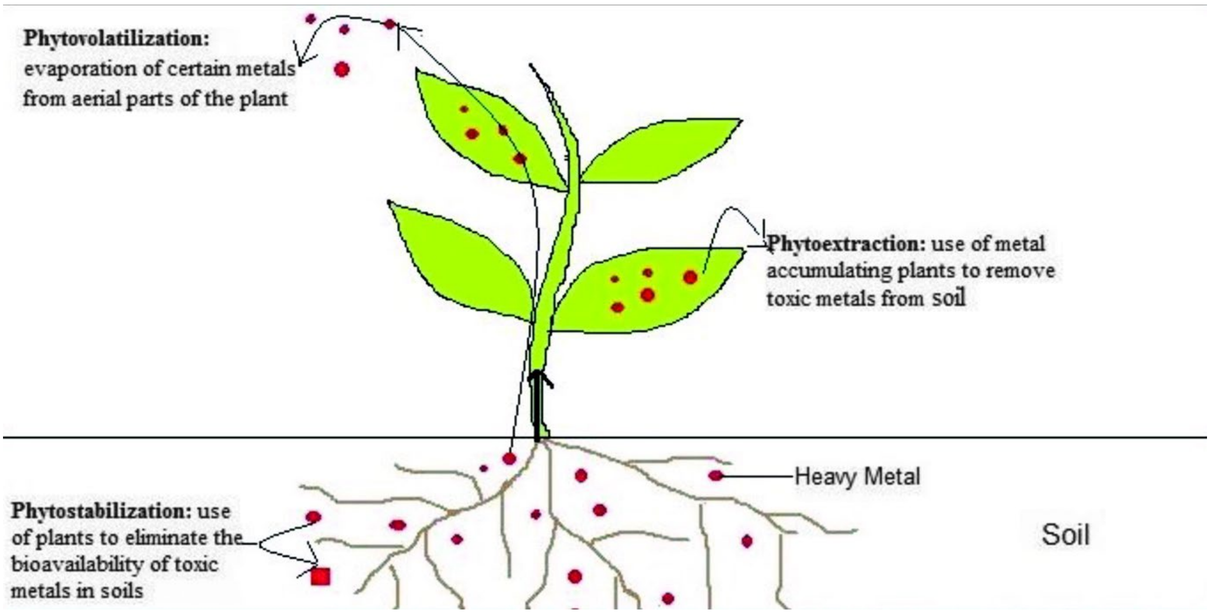


Figure 2. 1. Schematic representation of different phytoremediation approaches in soils (Kushwaha et al., 2015)

2.4.5.2.1 Phytostabilization

During phytostabilization, plants are utilized to decrease metal mobility and bioavailability in soils via a stabilization mechanism (Sylvain et al., 2016). It is important to note that this process does not decrease metal concentration in contaminated sites. It merely renders metals non-motile and reduce metal off site movement thereby making them less harmful. Because the metals are restricted to the vadose zone of plants through this process, it prohibits its mobility (Bolan et al., 2011). It differs from other forms of phytoremediation in that it does not remediate polluted soils, but it hinders the contamination of close areas. Where phytoextraction is not possible or desirable, this technique can be used. Plants achieve restricted metal movement through a number of processes: reduction in runoff due to presence of above ground biomass, reduction in erosion via stabilization of soils by plant roots and reduction of leaching due to upward water flow caused by plant transpiration (Khalid et al., 2017). Its advantage is that it does not generate secondary contaminated waste that would require further disposal or management. To retain the desired stabilized conditions, phytostabilized soils would require regular monitoring (Bolan et al., 2011). Ideal plants for phytostabilization are plants with capacity to accumulate high concentration of metals onto its root with limited translocation to its aerial parts (Ali et al., 2013). Plants such as *Festuca spp.* and *Agrostis spp.* have been identified as good phytostabilization plants of soils in Europe polluted with Zn, Cu and Pb (Galende et al., 2014). Phytostabilization can be used simultaneously with other remediation techniques to boost immobilization. Use of stabilizing microorganisms and other organic soil amendment treatments may be ideal (Rajkumar et al., 2013).

2.4.5.2.2 Phytovolatilization

Here, plants take up heavy metal contaminants from soil, converts and releases it to the atmosphere via transpiration as less toxic vapours. During this process, heavy metals are taken into volatile organic compounds but are released as biomolecules (Marques et al., 2009). This phytoremediation method is mainly ideal for only a select number of metal(loid)s that can exist in a gaseous state in the environment. For example, Hg (Ghosh & Singh, 2005), Se (Bañuelos and Mayland, 2000) and As (Sakakibara et al., 2010) have been shown to safely occur in the atmosphere in a volatilized state. *Brassica juncea* and *Arabidopsis thaliana* have been evidenced to grow under high concentrations of Se and with high capability of converting and volatilizing Se in the atmosphere (Bañuelos and Mayland, 2000). The process of converting heavy metals into a volatilized less toxic form in plants is via specified mechanisms controlled by specific genes or enzymes. Only a few naturally occurring plants are capable of optimal phytovolatilization. This technique is therefore aided or enhanced greatly by genetic modification of selected plant species (Meagher, 2000).

However, questions have been raised over the fate of these volatilized metal(loid)s in the atmosphere. Meagher (2000) though suggested that these volatile compounds are diluted and dispersed in the atmosphere and so pose little to no environmental threat.

2.4.5.2.3 Phytoextraction

Phytoextraction refers to the use of plants to clean up metal(loid)s by means of uptake. This technology is solar-based and depends a great deal on the plant root's capacity to take up metals, translocate to its aboveground parts for retention. This process leads to the decrease in metal concentration in soil and concentration of metal contaminants in the above ground parts of plants. While this technology guarantees the removal of metals from soils, its suitability is limited to low to moderate level of metal contamination as plant species are not capable of sustaining high levels of metal contamination for long period of time (Sabir et al., 2015). Plants capable of accumulating high concentration of metal contamination into their shoot tissues with little to no visible toxicity consequence are generally referred to as hyperaccumulators (Ali et al., 2013).

Hyperaccumulator plants have some general suitability characteristics such as (a) high growth rate with high biomass production, (b) high metal tolerance threshold, (c) ability to concentrate high volumes of heavy metal into its above ground tissues and (d) good rooting system (Khalid et al., 2017). To satisfy the criteria for being named hyperaccumulators, plants must be able to take up large volumes of metal contaminants and still able to thrive. What constitute 'large volumes' differ for different authors, and it also depends greatly on the kind of metals. Brooks et al. (1977) establish their threshold at > 1000 mg/kg for Ni. Other authors opined that hyperaccumulator plants should have a capacity to accumulate metals 100 – 500 fold higher than the amount accumulated by non-hyperaccumulator plants with little to no effect on its productivity (Sheoran et al., 2016; Mahar et al., 2016).

The advantages of phytoextraction over some other traditional remediation methods are (a) reduced disruption to soil and the environment, (b) very economical, (c) disposal site not required, (d) ideal for multi-metal contaminated areas, (e) Excavation and transportation of metal contaminated soils not required (Sheoran et al., 2016). It also has its limitations which are (a) very dependent on growing conditions of hyperaccumulator plants/microorganisms, (b) very dependent on plants tolerance to metal accumulation (c) relatively slower pace of remediation (Khalid et al., 2017). Other limitations of phytoextraction are that it only extracts bioavailable fractions of metal contaminants, negative stakeholder acceptability, the need to implement long-term field trials to ascertain the veracity of the technology and the need to incorporate wider value propositions into remediation decision management (Moreira et al., 2021). Additionally, phytoextraction only removes the bioavailable fractions of heavy metals in soils and not the total metal concentration, hence the need to incorporate a more risk-based approach to contaminated land management which focuses on limiting contamination risks as against management schemes aiming at completely removing total metal concentrations from soil.

The significance of phytoextraction as a remediation method cannot be overstated but careful attention should be paid to developing a sound methodology and considerable technical expertise especially when dealing with large scale tasks.

The process of phytoremediation can be aided by several additional modifications to increase plant metal uptake capacity. Some of such modifications are, optimal agronomic management practices, genetic engineering, chelate aided phytoremediation and microbial assisted phytoremediation.

- **Genetic engineering of plants**

Some specific genes are involved in some plant physiological response like metal uptake, translocation to shoots and sequestering metals in plant vacuoles. When identified, these genes can be transferred to plant candidates of interest to improve its phytoremediation capabilities. Genes targeted should be in line with desired objective. For example, if the desired outcome is improved phytostabilization, genes of interest would be ones that enhance uptake of metals and sequestration of metals in plant roots. This technology is being used increasingly in plant science to improve specific plant properties of interest (Clark & Pazdernik, 2015; Kafle et al., 2022).

- **Chelate aided phytoremediation**

The process of phytoextraction is very dependent on metal bioavailability and is considered very time consuming in comparison with other physico-chemical remediation technologies. This can greatly limit the applicability of phytoextraction as an efficient remediation technique. Over the last decade, chelate-assisted phytoextraction has gained prominence as a solution to the problem of metal bioavailability and has been shown to greatly enhance the rates of plants metal uptake and translocation (Saifullah et al., 2009; Evangelou et al., 2007). Chelating agents identified in the literature include humic substances, elemental sulfur, hydroxyethylene diamine triacetic acid (HEDTA), nitrilo triacetic acid (NTA), ethylene diamine tetraacetic acid (EDTA), low molecular weight organic acids (LMWOAs), ethylenediamine-N, N'-disuccinic acid (EDDS) and ammonium fertilizers (Saifullah et al., 2015; Shahid et al., 2012).

Regardless of the well documented effectiveness of chelate-aided phytoremediation technology, there are persisting concerns about the environmental ramifications of the use of some chelating agents. For example, there are concerns about the use of EDTA due to its potential effects on soil microorganisms, groundwater contamination and issues relating to low decomposition (Cay et al., 2016). Owing to these environmental issues associated with the use of EDTA, NTA and EDDS are proposed as more environmentally friendly alternatives, even though they are possibly less effective. In general, the usage of this variant of phytoremediation has not garnered sufficient public acceptance due to limited efficiency, high running costs and potential leaching risks.

- **Microbial assisted phytoremediation**

Given the limitations of phytoremediation mentioned earlier in section 1.1, microbial-assisted phytoremediation is also a promising technology to remediate soils safely and efficiently from metal contamination. Microbial remediation can be a stand-alone technology that seeks to utilize microorganisms to induce absorption, oxidation, and a general reduction of metal(loid)s in soils. In association with plants, soil microorganisms can potentially promote plant growth and improve plants tolerance to metal stress (Khalid et al., 2017). These are generally referred to as plant growth promoting microorganisms. It is very established in the literature that some soil microorganisms not only aid plants growth, but also aid in protecting plants against adverse effects of metal contamination as well as positively impacting metal accumulation in hyperaccumulator plants (Weyens et al., 2009; Bhanse et al., 2022). Mechanisms of this technique include bioleaching and biomineralization, biosorption, enzyme-catalyzed transformation, redox reactions, and intracellular accumulation (Lloyd, 2002, Bhanse et al., 2022). Metal-resistant rhizobacteria can induce the growth and stimulate metal-accumulation properties of plants via the production of substances like indole acetic acid (IAA), monocyclopropane-1-carboxylate (ACC) deaminase and siderophores (Rajkumar et al., 2012). These metal-resistant rhizobacteria can also enhance the metal tolerance properties of host plants by inducing superoxide dismutase, thiol compounds and metallothionein (Khalid et al., 2017).

Soil microorganisms can also aid bioavailability and metal mobility in soil via mechanisms such as production of compounds such as siderophores (known for their plant-promoting and metal-chelating properties), production of biosurfactants by alteration of soil redox conditions and lowering of soil pH (Ullah et al., 2015). However, the effects of microorganisms on plant accumulating properties of plants vary on case-by-case basis as there are studies that have shown where metal uptake have reduced due to the effects of some soil microorganisms (Ma et al., 2015; Ahemad, 2019). It is therefore important to explore options based on the given specific circumstance before adopting this method as a remediation technique.

To make informed decision on the remediation technique to adopt for the remediation of metal contaminated soil, certain factors need to be put into consideration. One should consider the cost of running the technology, the effectiveness of the technology under high metal contamination levels, the time required to attain targeted levels of clean-up, its applicability on multi-metal contaminated sites, long-term effectiveness, and commercial viability of the technology. For this study however, phytoextraction is the technology of interest and this process is largely driven by the use of metal accumulators as described in section 2.4.5.2.3.

2.5 Metal accumulator plants of interest

As will be detailed in section 3.2 of chapter 3, metal accumulator plants of interest for this study are: *Brassica juncea* (Indian mustard), *Glycine max* (soybean), *Helianthus annuus* (sunflower), *Miscanthus sinensis* (silvergrass), *Panicum virgatum* (switchgrass), *Salix spp.* (willow), *Populus spp.* (poplar), and *Typha latifolia* (cattails). They are 8 of the most widely and commonly researched species based on the systematic review carried out in section 3.2.

2.5.1 *Brassica juncea* (Indian mustard)

The rapeseed-mustard (*Brassica spp*.) is one of the world's most important oilseed crops; surpassed only by Soybean *(Glycine max)* in terms of global production. Global production of

Brassica spp. and its oil is estimated at 12 – 14 million megatonne (Mt) respectively (Bindhani et al., 2020). *B. juncea* is grown mainly under temperate climatic conditions but have been reported to grow well under tropical and subtropical conditions as a cold weather crop. They can tolerate annual precipitation distribution range of 500 to 4200mm and annual temperature ranging from 6 to 27°C, preferring pH from 4.3 to 8.3 (Shekhawat et al., 2012). They are crops with high oil content and of high quality, high yield potential (1500 – 3000 Kg/ha) and very good adaptability (Shekhawat et al., 2012). *B. juncea* has been described as a hyperaccumulator plant by Salt et al. (1996), Jiang et al. (2000) and more recently Halder & Anirban (2021) for their importance in the removal of toxic metals from the environment and for their fast growth rate and biomass production.

2.5.2 *Glycine max* (Soybean)

The soybean is an annual leguminous crop of Chinese origin. It's a crop well adapted to different soil types but thrive best in well drained soils with pH ranging from 6.5 to 7 (Fehr, 1980). They are primarily cultivated for protein and oil production but are very good source of feedstock for feed, fuel, biobased products and even food. As a result of increase in agronomic technology, the global production of soybean has increased in the past decade from 155.1 million Mt in 1999 to 201.9 million Mt in 2009 (Pratap et al., 2012). Current global production is at 384.01 million Mt (USDA, 2021). Soybean occupies the premier position of oilseed crops in terms of global production amounting to about 53% of global oilseed production share (Pratap et al., 2012). They are also reported to be very effective for phytoextraction of metals to clean up metal toxicity in the environment with reported removal rates ranging from 23.0 – 77.06% (Murakami & AE, 2009; Morar et al., 2018).

2.5.3 *Helianthus anuus* (Sunflower)

Sunflower is also one of world's most important oilseed crop. The short-season crop is of North American origin and can be cultivated over a wide range of latitudes in clear contrast to other oilseed crops. Breeding efforts over the years have resulted in higher yielding varieties of seed and oil and it is currently the third most produced oilseed crop in the world with around 56.01 million Mt per annum (USDA, 2021). Even though sunflower is a moderately drought resistant crop (Hussain et al., 2018), they prefer moist well drained fertile soils with heavy mulch and optimal soil pH range around 6.0 – 7.5 (Schoch et al., 2020). They have been shown to have huge hyperaccumulation properties for managing toxic heavy metal pollution in the environment (January & Cutright, 2008).

2.5.4 *Miscanthus sinensis* (Silvergrass)

Silvergrass is a perennial rhizomatous grass plant with origins from Asia. It was grown originally as an ornamental plant since the 1800s and is currently considered a very promising bioenergy plant species. It is a sturdy plant grown from seeds or propagated via rhizome division/micropropagation and has the capacity to thrive in a wide range of soil types ranging from sand to soils rich in organic matter with ideal pH range at 5 - 7.5 (DEFRA, 2007). While they are susceptible to pests and diseases in Asia (area of origin), these kinds and levels of infestations are yet to be experienced or reported in the UK (DEFRA, 2007). With a net calorific value of 17MJ/kg, silvergrass can be used for small scale heat production, for co-firing in coal power stations and can help bolster large-scale electricity power stations (DEFRA, 2019). Silvergrass have also been demonstrated to be a good phytoremediation crop for metal extraction in soils (Bang et al., 2015; Yadav et al., 2021).

2.5.5 *Panicum virgatum* (Switchgrass)

Switchgrass is also a perennial warm season rhizomatous grass plant. It originated from North America and used primarily as an ornamental plant as well as for game cover and for soil conservation (Vogel et al., 2011). More recently however, it has been used as a biomass crop for ethanol and butanol production, as an agent for biosequestration of carbon dioxide present in the atmosphere and have also been used for electricity and heat production (Mazur et al., 2020). Switchgrass can be cultivated on a wide range of soils ranging from sand to clay loams but for optimal performance, well drained fine-textured soil with pH around 5 – 8 is recommended (Casler et al., 2011). They can also tolerate low soil nutrient and some levels of drought (Adkins et al., 2016) Switchgrass has been exposed to many screening as a potential crop for biofuel production and it has been identified as a major promising plant for use as feedstock for biofuel conversion (Parrish & Fike, 2005; Mclaughlin & Kszos., 2005). In addition to its bioenergy benefits, switchgrass have also been shown to be good metal remediation plants (Patela and Pandey, 2020; Li et al., 2011; Jeke et al., 2017).

2.5.6 *Salix spp.* (Willow)

Willows are deciduous trees and shrubs usually found in most soils of temperate regions in the northern hemisphere. They are earlier grown primarily for its usefulness in manufacturing products likes chairs, cricket bats, craft papers, baskets etc. but are very useful for environmental efforts relating to conservation and erosion control as well as medicine and food (Mleczek et al., 2010). They are also a high yielding species. There have been reports of fertilized and irrigated willow grown in 3-year rotations with yields of over 27 oven dry tonne per hectare (odt/ha/yr.) in North America (Adegbidi et al., 2003) and about 30 odt/ha/yr. reported in Europe (Christersson et al., 1993).

They have been identified as important species for sorption and tolerance against heavy metals due to their capacity to thrive under metal stress. Important features which make them desirable energy and phytoextraction plants are: high biomass productivity, tolerance, and capacity to adapt to soil impurities, capacity to selectively accumulate contaminants and amenability to new environmental conditions (Rosselli et al., 2003; Dickinson & Pulford, 2005).

2.5.7 *Populus spp*. (Poplar)

As a short rotation coppice crop, poplar has many advantages. Its juvenile growth rate is very rapid, it makes for a good coppice plant with good resprout ability and relatively easy to propagate vegetatively (Dillen et al., 2010). They originate from North America but currently widely distributed across Europe, Northern Africa to Asia. They are also capable of thriving under different soil types and climates (Baldantoni et al., 2014). They are used primarily as raw materials for making doors, papers, plywood, adhesives and biochemicals. However, they have been shown to have huge potentials for use in carbon sequestration (Hansen, 1993), phytoremediation (Sebastiani et al., 2004) and bioenergy generation (Coleman & Stanturf, 2006). Some species of poplar have been reported to survive in heavy metal contaminated soils and still produce high biomass (Giachetti & Sebasticani, 2006; Castiglione et al., 2009).

Poplars are generally regarded as good energy crops because of their capacity to generate high biomass yield (Sebastiani et al., 2004) and its lignocellulosic composition makes it ideal for bioethanol production (Sannigrahi et al., 2010). In addition, its high heating value, reduced ash content and lignocellulosic composition also makes them a promising source of thermal energy via biomass combustion (Chalot et al., 2012; Sannigrahi et al., 2010).

2.5.8 *Typha latifolia* (Cattails)

Cattails is a rhizomatous perennial aquatic plant that is rooted in the soil. It grows as an emergent in shallow water and on exposed soils at the edges of canals, ponds, ditches, lakes and sometimes even by streams and rivers even though this happens less frequently. They are native to North and South America but distributed well across Africa, Europe, and Eurasia. Cattails can thrive in several climates including northern and southern temperate, tropical, and subtropical, dry continental and, humid coastal (Gucker, 2008). They can also thrive in different soil types such as silt, clay, loam, and sand substrates with tolerable soil pH ranging from 5.7 to 7.2 and have thrived with pH of up to 9.2 (Lieffers, 1983). They can also thrive with fluctuating water levels and can withstand some level of flooding, at the same time they have also been described as fairly drought tolerant (Shay et al., 1986).

An in-depth lignocellulosic composition analysis of Typha suggest it is a promising crop for use as biofuel feedstock (Rebaque et al., 2017). Cattails have also been reported to show good metal tolerance and effectiveness in reducing menacing levels of heavy metals and biosolids in soils and water bodies (Jeke et al., 2017).

2.6 Multicriteria decision analysis application for phytoremediation

Environmental decisions are hardly simple. Its complex nature means information needs to be drawn from multiple disciplines incorporating natural, social, and physical sciences as well as from politics and ethics to reach an optimal decision (Huang et al., 2011). When there are range of decision options especially regarding remediation, some form of decision support techniques (DSTs) may be required to aid the user make the most optimal decision given specific objectives. Decision support has been defined as *"the assistance for, substantiation and corroboration of, an act or a result of deciding; typically, this deciding will be a determination of an optimal or best approach"* (Bardos et al., 2001).

Over the years, a wide range of common decision support tools have been utilized for land contamination management (CLARINET, 2002). These techniques are Life Cycle Analysis (LCA), Cost Effectiveness Analysis (CEA), Cost-Benefit Analysis (CBA) and Multicriteria Decision Analysis (MCDA). Onwubuya et al. (2009) reported lack of knowledge on DSTs, insufficient detail on options and generic nature of existing tools as limitations to application of DSTs. Onwunbuya et al. (2009) also stressed the need for ease of use of these DSTs thus recommending a tiered approach which represents a simple and valid approach, incorporating sustainability standards. To encourage its use, it is recommended that gentle remediation-based DSTs should adopt the form of a simplistic checklist or a decision matrix (preferably integrated into existing national framework guidelines) at alternatives appraisal stage (Onwubuya et al., 2009). Multicriteria decision analysis is generally favoured for its clarity, transparency, meticulous structure, and its thorough appraisal of options (Carlon et al., 2006). It is also favoured to provide adequate structure for a synergistic consideration of economic, environmental, and technological factors necessary for the assessment and selection of decision alternatives and for coordinating stakeholder involvement in decision processes (Kiker et al., 2005).

Multicriteria decision analysis (MCDA) lays out a methodical procedure to aggregate multidisciplinary inputs, inculcating cost/benefit considerations and stakeholder priorities to rank alternatives and make decisions (Wang et al., 2019). Some important MCDA methods are weighted sum model (WSM), weighted product model (WPM), Analytic Hierarchy Process (AHP) and Technique for Order of Preference by Similarity to Ideal Solutions (TOPSIS).

WSM is the simplest and one of the most used MCDA approaches where the sum of the performance weights is applied to performance scores of individual alternatives and on all criteria to determine the optimal alternative (Andianggara et al., 2019). Its advantage lies in its capacity to make judgement more accurately due to it been based on pre-defined values and preference weight (Putra & Punggara, 2018). A major drawback is that sometimes it can be prone to data dependency bias (Tofallis, 2014). WPM on the other hand uses multiplication instead of additions where the score of each alternative is raised by the corresponding criteria’s weight (Putra & Punggara, 2018). It eliminates the problem of data dependency and can provide value and cost to the value of the alternatives, but it is limited in that its interpretation of weight is less intuitive than WSM (Putra & Punggara, 2018). They show the exponential relative importance, and not proportional between variables (El Amine et al., 2014). AHP decentralizes decision problems into a hierarchy of simpler subproblems and treated independently (Velasquez & Hester, 2013). It uses pairwise comparison to adequately compare alternatives as well as estimate criteria weight, but it is sometimes prone to self-assessment bias that can potentially affect internal validity (Velasquez & Hester, 2013). TOPSIS is based on the principle of selecting the alternative with the shortest geometric distance to the positive ideal solution and the longest geometric distance to the negative ideal solution (Qin et al., 2008). Its advantage is that it is simple and easy to programme and use and the number of steps does not change regardless of the number of criteria, but it is limited in that it is difficult to weight suitability criteria and keep consistency of judgment especially with additional criteria (Velasquez & Hester, 2013).

The application of MCDA in phytoremediation framework is increasingly gaining traction. In one of the earliest applications of MCDA to contamination management, Janikowski et al. (2000) utilizes a multilateral pairwise approach to examine options for contaminated land management in Katowice District in Poland and concluded that the two best management options are deep ploughing and phytoremediation, together with wilful and controlled cultivation.

Witters et al. (2009) using an MCDA compared the performance of willow, energy maize and rapeseed based on four criteria which are: metal accumulation capacity, agricultural acceptance, potential for CO_2 emission avoidance and gross agricultural income per hectare and concluded that even though short rotation coppice willow outperforms the alternative options in most categories assessed, its applicability in the short term is unlikely due to lack of short-term financial incentives for local farmers growing them.

More recently, Wang et al. (2019) utilized two MCDA methods, AHP and TOPSIS based on three criteria (Plants physiological characteristics, natural environment conditions, polluted soil properties) to assess plant selection for the phytoremediation of petroleum contaminated soils in two shale gas fields in China and reported that *Testuca arundinacea* was the most ideal plant for the phytoremediation of petroleum contaminated soils.

Lu et al. (2019) evaluated planting patterns to attain optimal contaminant phytoremediation using MCDA. Nine planting patterns were designed using plant species like *Setaria viridis, Echinochloa crus-galli* and *Phragmites australis* and cropping systems such as monocropping, double intercropping and triple intercropping. Criteria employed are metal absorption capacity, residual contaminant concentrations, investment cost, heavy metal root tolerance and concluded that triple intercropping involving the three plants was the most ideal planting pattern for optimal remediation.

Farzi et al. (2020) uses the TOPSIS MCDA method to screen 12 plants in the Chenopodiaceae family for their phytodesalination capacity. Criteria employed in this study were salinity mechanism, biomass production, geographical distribution in Iran, and flowering time. Plant species performances were weighted and ranked and *Salsola kali, Bassia moricata* and *Atriplex tatarica* emerged as the top performers of all the 12 plants assessed.

Mohebian et al. (2022) evaluating for phytoremediation optimization for heavy metal and petroleum contaminated soils used a combination of Structural Equation Modeling (SEM) and MCDA Analytic Network Process (ANP) (a variation of the AHP but using network instead of hierarchy) to assess the most influential factors for phytoremediation and compared different plants performance alongside different soil textures to optimize phytoremediation of mixed contaminated soils. From the result synthesis, the study reported that *Medicago sativa* was ideal and fit for purpose and sandy clay loam is the most suitable texture for phytoremediation measures.

Even though most phytoremediation-based application of MCDA in the literature are very case-specific and not holistic, its significance in decision making for remediation purposes cannot be excessively stressed as it presents a pathway to evaluating conflicting factors that influence the application of the technology and informs decision makers on the merits and demerits of alternatives. The choice of MCDA approach is important for deciding the optimal decision and choice should be based on the nature of the decision problem and the areas of application (Velasquez & Hester, 2013). Because of deficiencies in some methods, it is now commonplace to combine MCDA methods to address deficiencies of specific methods (Wang et al., 2019). However, these methods can also be applied in their original form with great success if there is an adequate assessment of their strengths and weaknesses (Velasquez & Hester, 2013).

2.7 Biomass valorization for energy

Non-renewable energy consumption is the chief cause of carbon emissions, and this invariably leads to global warming associated consequences (Rijo et al., 2021). The recently conducted 2021 United Nations Climate Change Conference, COP26 sets an ambitious target of 25% reduction in carbon emissions by 2030 (UNFCCC, 2021). To achieve this, there must be a swift transition from fossil fuels to renewable alternatives. The finite nature of fossil fuels and the climate associated challenges it presents has made renewable energy technology even more appealing (Gielen et al., 2019). Important renewable energy sources include solar energy, geothermal energy, wind energy, hydropower, and biomass. They are referred to as renewables because they can be replenished naturally.

Biomass is considered a clean, abundant, and renewable source of energy that is viewed as a viable organic substitute for the more destructive fossil fuel due to its potential to produce liquid chemicals (Gustavsson & Svenningsson, 1996). Biomass is referred to as any renewable organic material that can be derived from plants and animals (EIA, 2021). These include, wood and wood processing wastes, agricultural crops and waste materials, biogenic materials in municipal solid waste, animal manure and human sewage. The use of biomass as an energy source is increasing especially in developed countries for use as transportation fuel and to generate electricity. In 2020, biomass accounts for almost 5 quadrillion British thermal units (Btu) representing about 5% of US primary energy consumption (EIA, 2021). Consuming sectors of this energy derived from biomass include industrial, transportation, residential, electric power and commercial. The process of obtaining value from biomass in the form of renewable energy is what is referred to as biomass valorisation (Pfab et al., 2019). Biomass is valorized to generate energy via the following processes:

- Direct combustion to produce heat energy
- Thermochemical conversion to produce fuel (Solid, liquid, and gaseous)
- Biological conversion for producing liquid and gaseous fuels

- Chemical conversion for producing liquid fuels.

In addition to these direct biomass valorization benefits, by-products from these processes can also be utilized to derive more value.

2.7.1 Direct combustion of biomass

The solar energy absorbed by plants from the sun helps drive the process of photosynthesis which enables plants to live and thrive. This stored solar energy in plants (and the waste they produce) is referred to as biomass energy. One way to recover this energy is by burning biomass as a fuel (Tewfik, 2004). Some important features of biomass are that they can be economically produced in mass with little environmental consequences, and they are very abundant. Biomass also fix carbon dioxide in the atmosphere via the process of photosynthesis. While other biomass thermo-chemical conversion technologies are increasingly gaining traction, direct combustion of biomass still accounts for more than 95% of global bioenergy production (Demirbas, 2004). This is boosted by the traditional use of biomass for cooking and heating especially in rural settings of underdeveloped and developing countries.

Earth's total live biomass is estimated at about 550 – 560 gigatons of carbon, mostly from growth of wild plants (Bar-On et al., 2018) and this renewable resource represents about 35% of primary energy consumption in developing countries (Demirbas, 2007). Its successful application in developing countries indicate its future potential to provide a sustainable and cost-effective source of energy as well as aiding countries meet their emissions reduction goals (Demirbas, 2007; Solarin et al., 2018).

Biomass combustion describes a series of chemical reaction which involves the oxidization of carbon to carbon dioxide and the oxidation of hydrogen to water. A deficiency in oxygen will lead to incomplete combustion and the consequent formation of associated products of incomplete combustion. The oxygen requirement is highly dependent upon the chemical and physical properties of the fuel. The combustion of the biomass is proportional to the combustion products, the burn rate of the fuel, the necessary excess air needed for complete combustion and the temperature of the fuel (Demirbas, 2007).

Characteristics of biomass influencing combustion are (i) ash content (ii) specific gravity and particle size (iii) extractive content (iv) moisture content (v) elemental (C, H, O, N) content and (vi) biochemical composition (cellulose, hemicellulose, lignin).

On average, the ash content of wood is about 0.5% (Demirbas, 2002). The ash content of any given plant material is dependent on the type of plant and the kind of contamination of soil it has been grown on. Ash content is a critical factor to determine the calorific value of any given biomass; the higher the ash content of biomass, the less desirable it is as fuel (Demirbas, 2002). For a profitable combustion process, the desired biomass particle size should be about 0.6cm or more (Demirbas, 2007). Biomass is significantly less dense with a higher aspect ratio than coal and it is very difficult to reduce to smaller sizes.

Moisture in biomass is expected to reduce its calorific value (Demirbas, 2002). Moisture content varies from plant to plant. In wood species moisture content ranges from 41.27 to 70.20 (Demirbas, 2003). Moisture content is lowest in stems and more in roots and plant crowns.

Another important biomass feature affecting combustion is the extractive content. This describes the proportion of combustible organic material present in biomass (Kataki & Konwer, 2001). The heating value of plant parts devoid of extractive contents are found to be less than those with the extractive parts. The higher the extractive content in biomass, the more desirable it is as fuel (Demirbas, 2002).

The physical and chemical composition of fuel can also give an indication of its combustion capacity. There is a relationship between the heat content and oxidation states of natural fuels and carbon atoms generally trumps the small fractions of hydrogen content (Demirbas, 2007). The higher the carbon content of a woody biomass, the higher its heating value (Tilman, 1978). Biomass cell walls are made of cellulose, hemicellulose, and lignin. The heating value of biomass fuels increase with increasing lignin content.

2.7.2 Biological conversion for producing liquid and gaseous fuels

Biological conversion entails the use of fermentation to convert the biomass into ethanol and the production of renewable natural gas using anaerobic digestion (EIA, 2021). Ethanol is used as fuels for vehicles. Renewable natural gas (biomethane or biogas) is produced at sewage treatment plants (in anaerobic digesters), and during livestock and dairy processes (Silva et al., 2021). They can also be obtained from solid waste landfills. When treated properly, renewable natural gas can be a veritable like for like substitute for fossil fuel natural gas (EIA, 2021).

2.7.3 Chemical conversion for producing liquid fuels.

This is hinged greatly on the process of transesterification which involves the conversion of triacylglycerides from various feedstocks (waste cooking oil, nonedible oil seeds, animal fats) and single cell oils or microbial lipids into fatty acid methyl esters (FAME) which is then used to produce biodiesel in the presence of alcohol (Bardhan et al., 2022)

2.7.4 Thermochemical conversion to produce fuel

This describes a thermal degradation process which involves heating biomass feedstock materials in closed pressurized vessels at high temperatures to produce fuel and other products (Sikarwar et al., 2016). Thermochemical conversion include gasification and pyrolysis and they differ based on the amount of oxygen present and the process temperatures used during the conversion process (EIA, 2021).

2.7.4.1 Gasification

Gasification involves controlled heating of biomass from 800 – 900 ºC with the insertion of controlled amount of oxygen and/or steam into vessel to make carbon monoxide and synthetic gas or syngas rich in hydrogen (EIA, 2021). Growing biomass is known to remove carbon dioxide from the atmosphere; therefore, this method has a low net carbon emission especially when carried out in combination with carbon capture, storage, and utilization in the long term.

Biomass gasification consists of series of intricate processes beginning with drying the feedstock, then pyrolysis, followed by controlled partial combustion of intermediates, and gasification of resulting products (Sikarwar et al., 2016). The gasification process is carried out in the presence of a gasifying media like air, steam (H_2O), oxygen (O_2) or carbon dioxide (CO_2) inside a gasifying reactor (Sikarwar et al., 2016). The heating value of the gas products from the process depends very much on the gasifying agent in use. For example, the calorific value of the product gas in air gasification is around 4 – 7 MJ Nm^{-3} (Megajoules per normal cubic metre) but when gasifying agent like pure O_2 is utilized, calorific value can go as high as 12–28 MJ Nm^{-3} (Rapagnà et al., 2000). Besides the gasifying agents, other factors that affects the quality and properties of the gasification products are feedstock material and dimensions, reactor's temperature and pressure, reactor's design and the presence of sorbents and catalysts (Parthasarathy & Narayanan, 2014).

Multiple useful products can be derived from biomass gasification such as: synthetic gas (syngas), biofuels, power, heat, fertilizers, and biochar. Syngas can also be further subjected to additional processing via the Fischer-Tropsch process to convert to dimethyl ether, methanol, and other chemicals (Sikarwar et al., 2016). Gasification can accommodate different groups of biomass feedstocks such as herbaceous biomass, woody biomass, manures, and marine biomass (Basu, 2010). Gasification process usually involves designing the operational process to give a desired product and this is chiefly driven by the type of biomass feedstock used and any optimization employed where necessary.

Although the primary motivation of using biomass gasification is to boost resource efficiency by utilizing a wide variety of waste materials as feedstock and to mitigate CO2 emission rates, its application could also pose potential environmental risks. One such problem is the potential emission of particulate matter, carbon monoxide, oxides of sulphur (Sox), oxides of nitrogen (Nox) and volatile organics (San Miguel et al., 2012). When exposed to humans via inhalation, ingestion and dermal contact, these pollutants can pose serious health risks (Kampa & Castanas, 2008). However, the effects are far less dire as emissions are very low (with an efficient gas clean-up and conditioning unit) in comparison to biomass combustion and fossil fuel combustion (Lewtas, 2007).

2.7.4.2 Pyrolysis

Energy from biomass are fuels that can be in forms of bio-solids, bioliquids and biogas and these different types of energy forms can be produced via different kinds of thermal conversion treatment. Pyrolysis is one of such conversion technology.

Pyrolysis is a term used to describe the thermal degradation of biomass in the absence of oxygen (Uddin et al., 2018). It is a process that entails the fissure of carbon-carbon bonds to the formation of carbon-oxygen bonds, with required standard temperature of about 400 – 550 °C and possibly higher in some cases (Chen et al., 2014). These processes occur within the pyrolysis reactor. The key difference of this process in relation to biomass combustion and gasification is that the process of thermal decomposition is carried out in the absence of oxygen. Its benefits among other thermal conversion technology are that there are less emissions released, it produces solid carbonized products (biochar), liquid products (bio-oils, tars), and gas products containing a mixture of CO_2, H_2, CO and CH_4 and all its by-products are reusable (Uddin et al., 2018). Any of these pyrolysis products can be maximized by adjustments to the conditions in the pyrolysis reactor (Santos et al., 2011). Broadly, there are three kinds of pyrolysis processes in practice: slow pyrolysis, fast pyrolysis, and flash pyrolysis (Uddin et al., 2018).

2.7.4.2.1 Slow pyrolysis

Slow pyrolysis prioritizes the production of charcoal at slow biomass heating temperature above 277°C and maximum temperature range of 677°C in the absence of oxygen (Laird et al., 2009). This pyrolysis variation is characterized by a longer residence time typically ranging from 5 to 30 minutes and a low heating rate of 5 to 7°C/minimum (Uddin et al., 2018). Here, biomass is slowly pyrolyzed at low heating rates with minimal production of the liquid and gaseous products and maximal production of char.

2.7.4.2.2 Fast pyrolysis

This is the most common of all the pyrolysis types and it prioritizes the production of bio-oil which is its major product. Biomass feedstock decomposes very rapidly generating minimal coal and gas and maximizes bio-oil production. Here, the rapid decomposition of the carbonaceous biomass is undertaken in the absence of oxygen at moderate to high heating rates (upwards of 10-200°C/s) with residence time at around 0.5 – 10 seconds and reactor temperature at ranging from around 577 – 977°C (Balat et al., 2009).

2.7.4.2.3 Flash pyrolysis

Compared to other pyrolysis variations, flash pyrolysis, or ultra-fast pyrolysis thermally decomposes biomass at extremely rapidly at higher heating rates (>727°C/s) with residence time lower than 0.5 s and reactor temperature at around 777 – 1027°C (Balat et al., 2009).

2.7.5 Pyrolysis products

As earlier mentioned, the products of pyrolysis are primarily char, gases, and condensed vapours which is transformed into viscous liquid (bio-oil) at room temperature.

2.7.5.1 Bio-oil

Bio oil, sometimes called pyrolysis oil is a viscous dark browned liquid derived from a pyrolysis process with similar elemental composition as the biomass (Uddin et al., 2018). It is the main product of fast and flash pyrolysis. It is a complex mixture of oxygenated compounds, water and in some cases, dissolved alkali, and coal particles from the generated ash. Its content composition is determined hugely by the biomass type, the apparatus, process conditions and how efficient the separation of the coal and condensed liquid was (Uddin et al., 2018).

While bio-oils can be used as fuels for boilers, engines, and turbines to generate heat and power, further modifications can be made to use as transport fuels and chemicals for industries (Demirbas, 2004). It is important to research more efficient optimization pathways in reactor design to maximize its production.

2.7.5.2 Biochar

Biochar is a term used to describe a substance made from the carbonization of organic material (also called biomass) under high temperature in the absence (or near absence of) oxygen. Its production is maximized when slow pyrolysis is adopted, and it is seen as an emerging avenue to improve food security in countries and mitigate climate change and its effects (Lehmann & Joseph, 2015). Its applicability is mainly associated to soil enrichment giving some benefits such as soil fertility improvement via soil pH alteration, nutrient retention via cation adsorption, reduction in greenhouse gas emissions, adsorption of toxic metals and organic pollutants, and productivity improvement (Mašek et al., 2013; Bolan et al., 2021).

2.7.5.3 Syngas

Syngas is a product of thermochemical conversion of organic materials. It is sometimes seen as an intermediate product because it can be further converted via different mechanisms to produce other forms of energy products such as electricity and high quality gaseous and liquid fuels used as transport fuels (Börjesson & Ahlgreen, 2012). When slow pyrolysis is adopted, about 10 – 35% of biogas is produced (Uddin et al., 2018).

The yield of syngas is greatly influenced by the pyrolysis temperature applied, and yield is maximized using flash pyrolysis at very high temperatures (Uddin et al., 2018). Kantarelis & Zabaniotou (2009) reported a 78.87% gas yield at 900°C using a downstream fixed bed pyrolysis reactor. Tang & Huang (2005) also reported a 76.64% syngas yield using flash pyrolysis in a radio frequency plasma pyrolysis reactor.

Syngas is mainly composed of carbon monoxide and hydrogen. It could also contain trace amounts of nitrogen, carbon dioxide, water, methane, ash, tar etc. its content depends greatly on the biomass feedstock used and the pyrolysis conditions they are exposed to (Fernández & Menéndez, 2011).

2.8 Combing phytoremediation with bioenergy production

Phytoremediation is a technology that has been in contemporary practice and is still a promising environmentally friendly way of dealing with metal contaminants. Its potential is yet to be fully explored. Incorporating biomass production to the process has made the technology even more appealing, as the utilization of biomass for fuels has been touted as one of the most attractive options for dealing with increasing energy demand globally. Dealing with metal-polluted biomass remains the critical issue with the process and this has been explored by many authors who has shown huge potential for the incorporation of phytoremediation with bioenergy generation as a synergistic process (Yadav et al., 2018; Dastyar et al., 2019; Ali et al., 2020).

Biomass derived from phytoremediation can be valorized economically to produce forms of bioenergy like biogas or biofuels (Gomes, 2012). However, the presence of contaminants in biomass presents potential risks relating to concerns around the contaminants being reintroduced back into the soil due to poor management and disposal practice (Edao, 2017). Hence the need for options like biomass pre-treatments to reduce pollutant motility and transfer or via the use of adsorbers.

To manage the problem of reincorporating pollutants back into the environment, Han et al. (2018) put forward the utilization of adsorption-pyrolysis technology as a means of recovering valuable metals from biomass after the phytoremediation process. Using *Broussonetia papyfera* biomass as their study material, the biomass was exposed to contaminated soil and water samples obtained from mining and smelting sites. They were exposed for 0 – 180 minutes and at a range of pH (2, 4 and 6) to maximize adsorption. After pyrolysis at 1000°C, the authors reported that metal-rich *B. papyfera* is a good recovery material for heavy metal via the adsorption-pyrolysis process and performance increases with increasing pH as the highest sorption value was observed at a pH of 6.0.

He et al. (2019) investigated the behaviour of 12 metal(loid)s present in *Avicennia marina* (obtained from phytoremediation) in pyrolysis products at temperatures ranging from 300 to 800°C. On analysis of the derived leachate from phytoremdiation-obtained biochar, they reported that pyrolysis was effective in the reduction of metal bioavailability and motility and that the biochar can be useful as potential soil amendments. Optimum pyrolysis temperature was reported as between 400°C to 500°C. the study also reported that the presence of metals in biomass had no negative effect and may well have indications of positive effects as it showed increased biochar and gas-yield with less bio-oil yield. As was stated earlier in section 2.5.4.2.1, slow pyrolysis supports increased char yield with reduced bio-oil yield.

Pre-treatment of biomass prior to pyrolysis is theoretically a way to influence pyrolysis product properties, the distribution of heavy metals during pyrolysis, and the stability of heavy metals in pyrolysis product. He et al. (2020) put the theory to test by utilizing *A. marina* obtained from phytoremediation and treated with ferric salts ($FeCl_3$ and $Fe(NO_3)_3$). The authors reported that the application of ferric salt treatments to metal-contaminated biomass catalysed the pyrolysis process, inhibited the bioavailability and motility of metals in biochar, allowed the running temperature at 500-700°C with little risks while optimally enabling a value-added successful phytoremediation-pyrolysis process.

In addition, when biomass undergoes combustion, many useful by-products can be derived from it, therefore this was tested by Pogrzeba et al. (2018). They investigated the suitability of *Sida hermaphrodita* (an energy crop) to phytoextract some heavy metals in soils and also carried out a follow-up gasification experiment with the derived biomass to determine its calorific value. The authors reported that *S. hermaphrodita* was useful to accumulate metals, but this is dependent on their bioavailability and fertilizer application caused a reduction of metal accumulation in plants. They reported a slight reduction in calorific value for contaminated plants when compared with the noncontaminated ones. Additionally, the authors concluded that the ashes from incineration can be safely used in agriculture and forestry as fertilizers especially in locations carrying out phytoremediation exercises.

The above-reviewed publications suggest the concept of linking phytoremediation with thermochemical conversion of biomass for fuel production has significant potential to foster sustainability by valorising contaminated biomass into biofuels free of metals and leaving by-products harm-free, at the same time allowing for metal recovery where necessary. However, this study aims to take it one step further by utilizing metal-enriched pyrolysis by-product (biochar) for wastewater treatment. Species also need to satisfy important criteria for both metal accumulation and bioenergy generation. Some important identified criteria from the literature are metal accumulation potential (Dotaniya et al., 2022), growth rate (Sanodiya et al., 2022), rooting system (Li et al., 2022), metal tolerance (Gülçin et al., 2021), biochemical composition (Sharma et al., 2022), biomass production (Rheay et al., 2021) and second generation attribute (Grifoni et al., 2021).

2.9 Biochars and their environmental significance

As described in section 2.7.5.2, biochars are a product of a controlled combustion process (pyrolysis) carried out in the absence of oxygen. Its source materials are usually exclusively limited to organic biological residues such as, crop residues, wood, poultry litter etc. These carbonaceous materials have capacity to absorb and retain plant nutrients in soil, therefore increasing soil fertility (Lehmann, 2007). This practice of incorporating biochar to topsoil is an ancient technology for the improvement of soil structure (Maroušek et al., 2017). The environmental potential of biochars have been continually explored over the last two decades to understand and identify its most efficient application conditions on case-specific basis. Studies have explored feedstock types (e.g., plant residues, sewage sludge, food waste etc.) (Zhao et al., 2019), process parameters (e.g., retention time, temperature, particle size, pre-treatments etc.) (Leng & Huang, 2018), and other environmental factors (e.g., pollutant types, lignin content etc.) (Singh et al., 2020). Overall, results have revealed the benefits around its usage and its potential for further exploration in real-time field applications. Its interaction with topsoil when used as sediments for soil improvement and stabilization are influenced by physical, biological, and chemical factors (Maroušek et al., 2015).

- **Physical factors**

It has been reported that biochar reduces soil bulk density, increases its soil water holding capacity and accelerates its permeability (Asai et al., 2009). Because biochar has lower bulk density than most mineral soils, therefore its application on soils tend to reduce the soil's overall bulk density (Verheijen et al., 2010). Low bulk density is an indicator of high soil porosity and reduced compaction which is beneficial for plant growth and yield (USDA, 2022). Also, the dusty and porous nature of biochar is beneficial for soil porosity and aeration in topsoil (Maroušek et al., 2017). Smetanová et al. (2013) also reported that the wettability of soils increases when incorporated with biochars, therefore reducing its erodibility. Verheijen et al. (2010) indicated that the water retention capacity of biochar enriched soils is influenced greatly by the connectivity and distribution of pores in the soil, which is influenced by soil structure, texture, and organic matter content.

Activated biochar generally consists of about 95% micropores having diameter less than 2 nanometre (nm). Since biochar porosity consists mainly of micropores, the quantity of additional water available for plants will be determined to a large extent by the feedstock type and the size of soil particles (soil texture) (Tseng & Tsen, 2006). The water storage benefit of biochar applications on soils will therefore depend greatly on modifications around the ratio of micro- meso- and macro- pores in the root zone of plants. In addition, application of dark carbonaceous biochar on topsoil increases the amount of solar energy absorbed (Krull et al., 2004), thus increasing soil temperatures which in turn increases soil biota activity and consequently increased vegetation period (Maroušek et al., 2015).

Reports suggests it is the porosity (average pore size distribution, particle size, specific volume, surface area etc.) that defines to a large extent the physical characteristics of biochars (Maroušek et al., 2017). Its application in soils may increase the net surface area of the soil and therefore act as an ideal substrate for a variety of soil micro animalia and micro flora (Chan et al., 2007). The structure carbon matrix of biochar with high porosity and extensive surface area is a veritable indicator of its potential as sorbent for managing and controlling environmental contaminants (Zhang et al., 2020). The physical characteristics of biochar (especially its surface area) are significantly influenced by the temperature dynamics experienced during the pyrolysis process (Leng et al., 2021).

♦ **Biological factors**

Soil productivity can be influenced greatly by activities of soil microorganisms. Fine biochar structure incorporated in soil can be a hub or refugia for beneficial soil microorganisms, such as bacteria or mycorrhizae and these can affect the binding of beneficial nutritive anions and cations (Atkinson et al., 2010). The soil is home to varied biological communities generally classified as algae, archaea, arthropods, bacteria, fungi, nematodes, protozoa and other invertebrates and their functions are varied and complex. Even within a biological community (e.g., fungi), functional groups within the community, i.e., pathogens, saprophytes and mycorrhizae may react differently to the application of biochar (Thies & Rilig, 2012). Generally, basal respiration and microbial efficiency in soils can be increased by biochar application, and there is evidence of increased N_2 fixation by symbiotic and free living diazotrophs due to biochar application in soil (Rondon et al., 2007). Mycorrhizal abundance (which can be linked to plant yield maximization) can also increase by biochar application which can be due to biochar effects in altering soil's physicochemical properties, or indirect effects on mycorrhizae as a result of its effects on other interacting microbes (Maroušek et al., 2017).

Jin (2010) observed an increase in microbial biomass with biochar application and opined that biochars may increase microbial carbon use efficiency which they attributed possibly to changes in the composition of microbial community caused by biochar application and an increased fungal to biochar ratio observed with soils with higher biochar content. Jin (2010) also reported an increase in P and N use in relation to C explained by changes to the dynamics of soil enzyme activities due to biochar application. The decreased activity of enzymes mineralizing C could possibly have contributed to labile C stabilization in biochar-containing soils. The increased need for P and N acquisition and the reduced need for C due to biochar application indicates a shift in microbial community composition and structure in soils with biochar. Bailey et al. (2011) on the other hand reported that application of biochar to soil biota resulted in a reduction of the activities of soil enzymes, indicating that the sorption reaction between biochar and substrates may have disrupted enzyme activities. The effects of biochar on soil enzymatic activities are varied but are usually linked to the interaction between biochar and soil biota of interest (Maroušek et al., 2017).

- **Chemical factors**

A well-known property of biochar is their tendency to increase soil's cation exchange capacity (CEC) and pH. When aged, biochar is high in CEC, thus enhancing its potential for use as binding agent for minerals and organic matter (Verheijen et al., 2010). However, when disintegrated by soil preparation practices and weathering, it is currently unknown how much changes will occur in biochar CEC. Increased CEC is usually caused by surface area increase for cation adsorption or charge density increase per unit surface of organic matter, which results in greater level of oxidation or a synergy of both scenarios (Atkinson et al., 2010). Similar to temperature effects on physical properties of biochar, process parameters typically influence the chemical properties of biochars and consequently influences their potential use (Sohi et al., 2010).

Its sorption capacity is one of the most beneficial attributes of biochar and it is determined greatly by the relative carbonized and non-carbonized fractions and their associated bulk and surface properties (Chen & Chen, 2009). Its affinity to organic compounds is 10 -1000 times stronger than to natural organic matter and it is regarded as a 'supersorbent' (Maroušek et al., 2017). Cederlund et al. (2016) reported adequate sorption of pesticides. De Jesus et al. (2017) reported that the application of biochars to soils improves its capacity to adsorb polycyclic aromatic hydrocarbons from soils. Other studies have shown successful immobilization of chlorine and other organic chemicals (such as polychlorinated biphenyl, phenols, and halogenated hydrocarbon) by biochars (Chen et al., 2019). Qiu et al., (2021) also reported that biochar application can also be effective for the immobilization and removal of heavy metals from soils. the study also showed that by modified partitioning of metals, their bioavailability and phytotoxicity can be significantly reduced. Kammann et al. (2015) also demonstrated improved capture and delivery of phosphate and nitrate anions by biochar application.

These properties of biochar highlighted its importance and promise as a material for waste management technology. Biodegradable waste can be converted to biochar as a recycling option and these biochars can be used to effectively remove contaminants from aqueous solution (Inyang et al., 2012; Ahmad et al., 2014).

2.9.1 Biochar for wastewater treatment

Given the highlighted problems associated with human misuse of natural resources, the consequent pollution associated with it has caused damage to water resources. Factories release dangerous effluents that pollute water resources with organic compounds, pesticides, detergents, and heavy metals (Abdolali et al., 2014; Verma et al., 2020). Consequently, there has been associated health effects to humans and other living organisms, as well as potential irreversible environmental damage. The removal of these contaminants is of utmost importance, but traditional means of clean-up are expensive and have been deemed to lack efficiency (Rangabhashiyam et al., 2014). Therefore, sustainable alternatives for wastewater treatment are continually sought.

Adsorption by biochar is an eco-friendly, economical, and efficient means of water treatment that is a veritable solution option for dealing with contaminants in water bodies (Abdolali et al., 2014). Biochars from agriculture are especially ideal as biosorption material as they come cheap and requires little processing to become useful (Thakur et al., 2022). They are advantageous in that they have high calorific value and are very available (Yaashika et al., 2019). They are considered efficient for removing contaminants from water, soils, and waste from effluents (Xiang et al., 2020). Feedstocks from agricultural residues contain hemicelluloses, cellulose, carbohydrates, protein, and lipids whose constituent functional group can be activated during the pyrolysis process to enhance their pollutant adsorption capacity (Qambrani et al., 2017).

The continual boom and development of the industrial sector has contributed immensely to the rapid proliferation in quantity and types of wastewater contaminants, making it a dominant source of wastewater contamination. Biochar has become a viable option for removal of contaminants from industrial wastewater, for both inorganic and organic compounds.

Dyes are an important environmental contaminant of concern as they constitute a large portion of industrial wastewater emanating from textile industries. Biochar treatment for these sets of contaminants is also favoured and some sorption successes have been reported with Pradhananga et al. (2017) reporting a favourable sorption efficiency using a nanoporous bamboo cane-derived biochar for the sorption of two sets of wool carpet dyes. Zazycki et al. (2018) also reported success utilizing a low-cost pecan nutshell biochar for the removal of Reactive Red from water.

Phenols and Polycyclic hydrocarbons (PAHs) are also emerging contaminants of concern in industrial wastewater. Chen & Yuan (2011) utilized biochar made from orange peel pyrolyzed at temperatures ranging from 150 – 700C to sorb 1-naphtol and naphthalene and demonstrated adsorption success up to saturation. Valili et al. (2013) also reported the favourable sorption capacity of biochar from malt spent rootlets pyrolyzed at 800 C, 2-folds above the raw materials. Using biochar produced from sewage sludge pyrolyzed at 500 C, Dos Reis et al. (2017) reported very high sorption capacity for hydroquinone removal.

To ascertain the technical feasibility of biochar as a sustainable treatment option for polluted wastewater, some important considerations are treatment efficiency, scale-up capability, process stability, ease of implementation, health, and safety considerations, as well as capacity to combine with other treatment techniques (Kamali et al., 2021).

- **Scale-up capability**

It is important that treatment technologies developed at lab-scales be able to transition to deal with more complex conditions in the presence of real-world effluents (Piccinno et al., 2016). There has been some successful application of larger scale optimization for biochar production process (Yi et al., 2018; Cuong et al., 2020). However, there is desire for more studies on the optimization of wastewater treatment using biochars. Also desired is the ability of the technology to combine with other treatment technologies at larger scales. He et al. (2018) in their review on biochar combination of standard municipal wastewater treatment concluded that such combinations are effective especially during colder seasons when the concentration of nutrients in effluents is higher because of reduced activity level of nitrifying and denitrifying bacteria in wastewaters with low temperature.

- **Process stability**

A major drawback of utilizing biological treatments is the problem of low stability when dealing with toxic non-biodegradable effluents such as those from pulp and paper mills (Kamali et al., 2019). The adsorption capacity of biochar depends greatly on their properties (for example, specific surface area). Biochars may lose their efficacy over time due to the occupation of their available surface area by pollutants over a period (Kamali et al., 2021). Therefore, an understanding of the properties of biochar-based materials is vital to avoid failures or any drop in performance.

The ease of implementation of the biochar technological process can also affect its stability and reliability. When the adoption of biochar technology is desired, efforts should be made to make the process, the facilities and equipment required to be less complicated to make the process more attractive for implementation.

♦ **Health and safety considerations**

Since the desire of most biochar-based treatment process for wastewater is to implement at larger scales, it is vital to prevent possible associated risks to workers and to attain its sustainability agenda. Whilst the route of human exposure to biochar has not been studied in any detail so far, the dust generated from biochar production can be very problematic and is seen as the predominant route for exposure of humans to biochar (Kamali et al., 2021). Like most dust particles, biochar dust may create toxic effects to the respiratory tracts but its effects on specific exposed organs is not well understood.

However, the presence of toxic elements in the biochar matrix may be a cause for concern when dealing with biochars. Controlling the production conditions and process may alter its overall effects and toxicity. Anyika et al. (2016) in a study assessing the concentration of toxic and non-toxic elements in biochars as it relates to the adopted production temperature. The authors reported that biochars produced under 650°C contains less toxic and non-toxic elements and there is therefore less exposure to any toxic effects of biochar production. Other factors like origin of the biochar origin (Devi & Saroha, 2014) can also contribute to the possibilities of toxic effects.

An ecotoxicological study on the effects of biochar on human liver, lung cell lines and on *Drosophilia melanogaster* (fruit fly) was carried out by Yang et al. (2019) and they reported that biochar effect on the viabilities of flies were negligible but has potential to inhibit cell growth. these studies are however insufficient to give a definitive statement of the effects of biochar on human bodies. However, adequate risk assessment should be carried out when embarking on large scale biochar projects and respiratory protective equipment should be worn during biochar production to reduce the risks associated with human exposure.

2.9.2 Efficiency of biochar treatment for heavy metals in wastewater

In addition to soils and sediments, water and wastewater treatment is an important fragment of carbonaceous materials application. Reports from recent studies have shown evidence of high levels of synthetic and emerging organic contaminants in aquatic systems (Petrie et al., 2014; Sorensen et al., 2015). These include personal care products, pharmaceuticals, dyes, and toxic pesticides. Studies have also reported persistent prevalence of inorganic pollutants on water environments (Li et al., 2017). When dealing with pollutants in water systems, adsorption is one recognized, fast, and universal treatment mechanism. It's a process where a substance (adsorbate) becomes attached to the surface of another (the adsorbent). Among available water treatment techniques, the process has been reported as one of the most efficient for treatment of water containing organic and inorganic contaminants (Rashed, 2013; Gwenzi et al., 2017). The use of different types of sorbents and their viabilities have been explored and have been effective at varying degrees (Gupta et al., 2009). It has also been shown that carbon-based adsorbents are the most cost-effective materials for the remediation of wastewater containing organic and inorganic pollutants (Ali, 2010). The use of activated carbon and other traditional techniques for remediation of contaminants in the aqueous phase comes at a high financial cost and concerns of the inevitable deposition of chemical residues with further environmental consequences and no economic value (Oliveira et al., 2017). Typical biochar has been identified as a low-cost carbon-based adsorbent with huge potential for sustainably removing organic and inorganic contaminants from aqueous solutions (Park et al., 2016).

Research efforts exploring the efficiency of various types of biochar feedstock for heavy metal removal in polluted streams has intensified in recent times. Niazi et al. (2018a) utilized pristine Japanese oak wood derived biochar for sorption studies involving arsenite (As(III)) and arsenate (As(V)). The authors reported higher sorption for As(V) than for As(III) at 84% and 81% respectively. When modifications were applied to the biochar, the authors reported that their capabilities were extended to handle concerning heavy metals. They concluded that heavy metal removal by this biochar is influenced by biochar origin, experimental conditions, and its modifications.

Adsorptive capacity of biochar for heavy metals is also determined greatly by the pyrolysis temperature adopted (Kamali et al., 2021). Niazi et al. (2018b) tested this theory using Perilla leaf-derived biochar and compared sorption effectiveness for biochars produced at 300°C and for those produced at 700°C for the removal of As(III) and As(V). The authors reported that biochars prepared at 700°C were more effective as adsorbents than ones produced at 300°C.

Reason given was the ones produced at 700°C have higher specific surface area and is surface aromaticity is more favourable for the adsorption of As than the ones produced at 300°C.

The influence of biochar modification on sorption properties of biochar was tested by Boshir et al. (2016) where they compared different kinds of biochar modification and their effectiveness for contaminant removal in wastewater. They reported that steam modification was not very effective in improving sorptive capacity of biochar, but chemical modification was much more effective. Boshir et al. (2016) opined that impregnation with nanomaterials and alkali treatment are the most effective techniques to improve adsorption capacity of biochar for environmental contaminants. The biochar's adsorption capacity and the adsorbate removal mechanism are greatly influenced by the type and concentration of the functional groups (such as -C-O, $-CH_3$, -OH, -COOH) present on the biochar surface (Qambrani et al., 2017). These functional groups are responsible for the surface complexation of the pollutants which results in their eventual removal from the contaminated media (Niazi et al., 2018a).

There are instances where the modification of the biochar structure can adversely affect certain properties (for example, the specific surface area), but still enhance the potential of biochars for certain desired outcomes. For example, even though clay integration onto the surface of the biochar may have reduced its specific surface area, its adsorption capacity was still increased considerably given the high ion exchange capacity of clay-based materials for several cations (Yao et al., 2014).
Another modification option applicable is the integration of magnetic compartments to biomass prior to pyrolysis. Yi et al. (2020) in their review concluded that the application of magnetic biochars in wastewater treatment can considerably improve its effectiveness against environmental contaminants. Tan et al. (2017) added magnetic composites Fe^{2+}/Fe^{3+} to rice straw prior to pyrolysis to form haematite (γ - Fe_2O_3), but still retaining the biochar functional groups, OH, COOH, C = O, C = C, and C-O-C. the authors reported that this integration of magnetic compartments significantly improved the adsorption of cadmium.

Effluents released by industrial facilities are usually laden with a mixture of different types of environmental contaminants. Therefore, a key parameter to gauge the efficiency of any treatment technique is its ability to remove a wide range of contaminants (Kamali et al., 2021). Studies on the production of high-quality biochar capable of simultaneously removing various heavy metals from water and wastewater is of high interest in the literature. This report will look to explore the simultaneous removal of competitive heavy metals using metal enriched sunflower-derived biochar. Choice of sunflower was based on the MCDA outcome from chapter 4. Additional details of biochar applicability for wastewater treatment and its application in this study is reported in chapter 6 of this thesis.

CHAPTER THREE

METHODOLOGY

3.1 Introduction

In the previous chapter, literature relevant to the overarching themes was reviewed and key knowledge gaps were identified which were highlighted in the introductory chapter of the report. In this chapter, focus is placed on the designed methodology to achieve the aim and objectives drawn from the identified research gaps. This chapter will explore the choice of materials, justification of methods where necessary, as well as experimental and analytical procedures. Data for this thesis were obtained from systematic reviews, greenhouse experiments, column experiments and subsequent laboratory analyses. The study was carried out in different strands where the findings of one phase feeds into the next (See Fig 3.1).

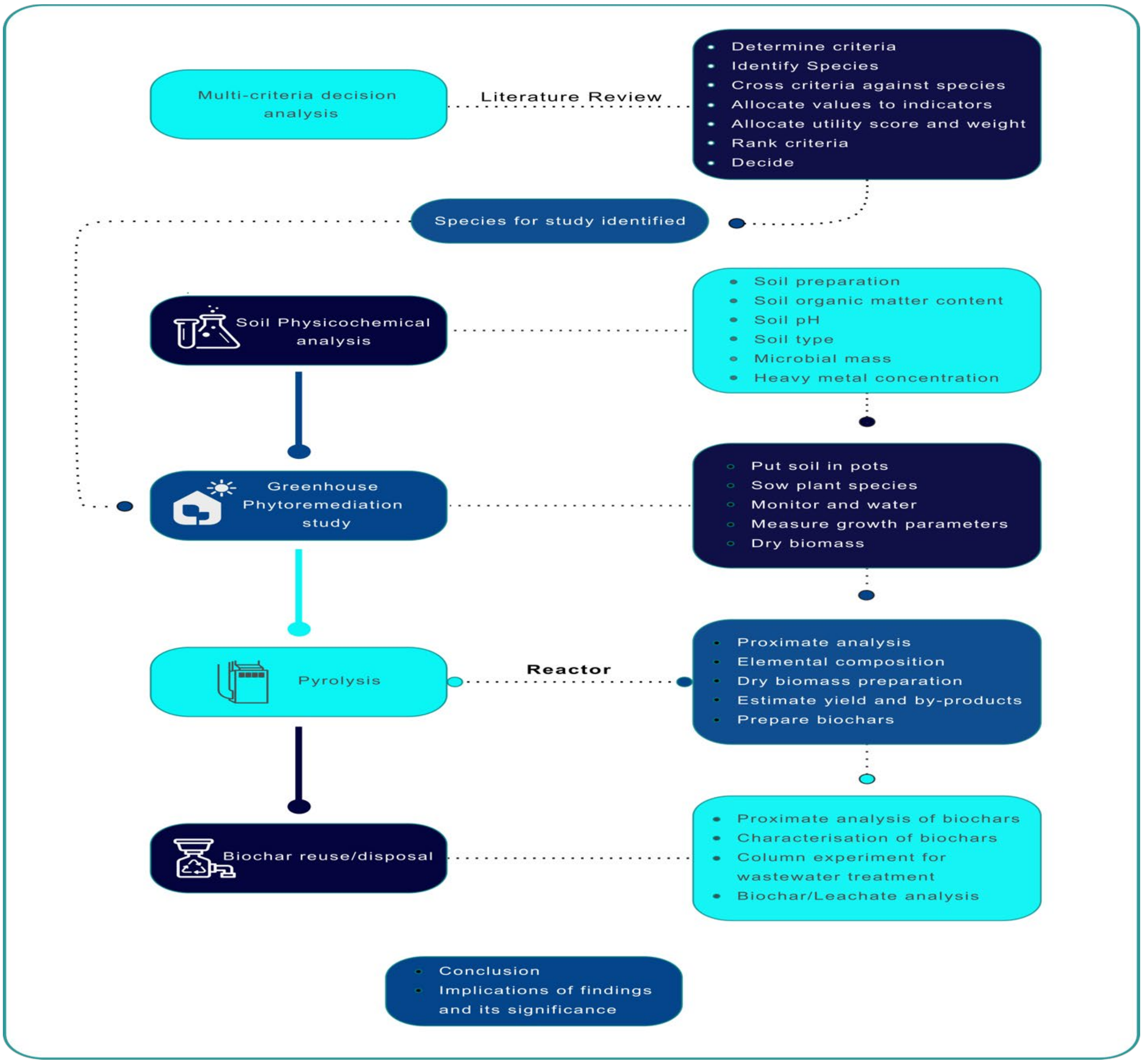


Figure 3. 1. Research methodology flowchart

3.2 Methodology for Multicriteria Decision Analysis

3.2.1 Systematic review protocol

An overview of different classifications of MCDA was elucidated in section 2.6 of chapter 2. The MCDA method employed in this research is the Weighted Sum Model or Simple Additive Weighting. This MCDA systematic review approach was adopted to measure value of different decision alternatives and making comparisons to get an optimum result. In broad terms, measuring value involves identifying specific decision problem, criteria selection, identifying candidates, measuring performance, scoring, weighting criteria, aggregation, and results interpretation (Thokala et al., 2016). Similarly, for this research, the processes employed for gathering information from the relevant databases are summarized in Table 3.1.

Table 3. 1 Overview of steps in Multicriteria decision analysis process

	Steps	Description
1.	Decision problem identification	Define objectives, identify type of decision, preliminary candidate screening
2.	Defining criteria	Identify criteria and performance index to evaluate performance
3.	Measuring performance by data	Gather relevant data from literature about the candidates under study
4.	Weighting criteria	Weight according to defined priority preferences
5	Aggregation	Compute performance data with criteria weightings to obtain an overall score for comparison
6	Results and interpretation	Record and interpret output to aid decision making

3.2.2 Defining the decision problem

A crucial part of this study is in selecting appropriate species that could be used for the synergistic process. The most suitable species should primarily have the capability to take up large amounts of metal contaminants into their tissues as well as possess adequate lignocellulosic properties. To elicit information to aid decision making about possible plant species, a preliminary selection process was adopted. These information about potential species were systematically sourced primarily from electronic scientific databases like SCOPUS, Clarivate Analytics' Web of Science and Google scholar. The procedure followed is a standard Preferred Reporting Items for Systematic Reviews and Meta Analyses (PRISMA) protocol as described by Moher et al. (2015). This is summarily illustrated in Figure 3.2. Key search words such as "phytoremediation crops," "hyperaccumulators" "bioenergy crops" "phytoremediation for heavy metals" were imputed into the search databases and gave accumulated hits of over 10,000. When these were narrowed to more targeted search terms such as "phytoremediation and bioenergy," "bioenergy crops for phytoremediation," the accumulated number of hits reduced drastically to 112. Careful analysis and synthesis of these articles from diverse journals which involved excluding articles unrelated to metal contaminants, excluding articles unrelated to energy considerations further reduced these articles to 76. From 76 hits, 29 species were most prominent and reoccurring. From these, 8 most widely and commonly researched species were selected, and these are: *Helianthus annuus* (sunflower), *Brassica juncea* (Indian mustard), *Glycine max* (soybean), *Miscanthus sinensis* (silvergrass), *Populus spp.* (poplar), *Salix spp.* (willow), *Panicum virgatum* (switchgrass) and *Typha latifolia* (cattails). Poplar and willow were considered at genus level while others at species level because of their woody characteristics. These species selected would be further exposed to more in-depth analysis informed by secondary literature to ascertain the most suitable for a synergistic phytoremediation study.

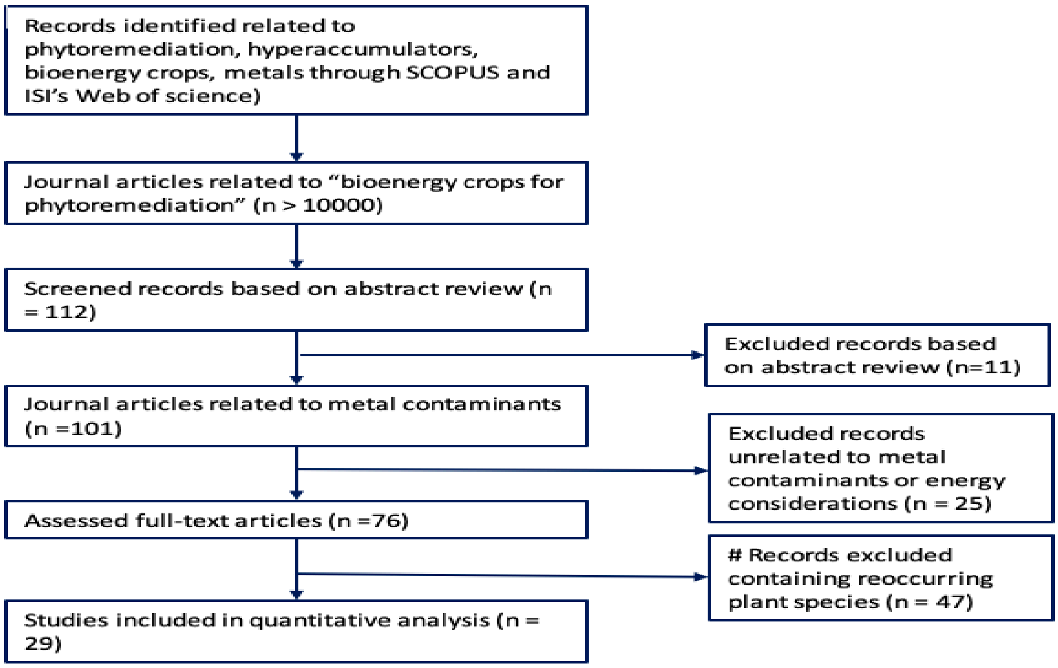


Figure 3. 2. PRISMA chart highlighting the systematic review process

3.2.3 Defining criteria/indicators

To effectively make decisions on any issue(s), it is vital to define suitability or performance criteria and describe how they relate to the parameters on which the decisions are to be made. Here, suitability criteria are defined as the major factors guiding a decision or judgment process (e.g., a species' hyperaccumulation potential reveals how good the species can be for phytoextraction). Criteria are backed up by key suitability indicators. Indicators here are defined as measures through which a species' individual suitability criteria can be evaluated (e.g., a good indicator for a species' hyperaccumulation potential is a translocation factor). In this study, only the most important indicator per criterion (as suggested by the literature) was selected as the barometer for comparisons. As indicated in section 2.8 of the literature review, selected suitability criteria used, and their associated indicators are highlighted in Table 3.2.

Table 3. 2 Suitability criteria and their key performance index

Criteria	**Key performance indicators (KPI)**	**Examples where these KPIs were used**
Pollutant accumulation	Translocation factor	Tangahu et al., 2011, Ramana et al., 2021a. Dotaniya et al., 2022
Growth rate	Crop growth rate (CGR)	Tangahu et al., 2011, Tanotra et al., 2022, Sanodiya et al., 2022
Root system	Root depth	Tripathi et al., 2016, Li et al., 2022
Metal tolerance	Metal tolerance index	Tangahu et al., 2011, Zvobgo et al., 2018; Gülçin et al., 2021

Biochemical composition	Lignocellulosic biomass	Pandey et al., 2016; Grifoni et al., 2021 Sharma et al., 2022
Second generation attribute	Competition with food uses	Tripathi et al., 2016; Thomas et al., 2022; Grifoni et al., 2021
Biomass production (tons per acre)	Total dry biomass (matter) yield	Tangahu et al., 2011; Afegbua & Batty, 2018; Rheay et al., 2021
Thermal energy potential	Calorific value in MJ per kg	Pandey et al., 2016; Angelova & Zapryanova, 2021; Grifoni et al., 2021
Drought tolerance	Yield index	Gavuzzi et al., 1997; Tripathi et al., 2016; Ramana et al., 2021b

3.2.4 Data collection for different criteria and KPIs

To collate information for the different established criteria, data were sought from published literature. Key databases utilized were the Clarivate Analytics' Web of Science database and the Scopus data base. Collating data from multiple sources can be a complex process. Factors and circumstances influencing results may differ, setting inclusion and exclusion criteria can be problematic and factoring time and spatial differences and how they could affect the output presents some challenges. Data were collected for the different categories, analysed and the means were calculated for simple performance comparison, and these were ranked. Unique exclusion criteria were set for the different suitability category as described in the subsections below:

3.2.4.1 Translocation factor (TF)

Bioconcentration factor and translocation factor are the common metric used to measure a plant species ability to accumulate contaminants (Takarina et al., 2017). While bioconcentration gives an indication of species' ability to remove contaminants from soil, the translocation factor gives an indication of species ability to transfer contaminants from roots to the aboveground part of plants. The desire of most phytoremediation process is to concentrate contaminants in the aboveground part of plants so this can be harvested away to attain adequate removal. This makes TF the key performance indicator. Also, species with high TF tends to have high bioconcentration factor (Takarina et al., 2017).

To gather scientific data for the translocation factor, the review protocol depicted in Figure 3.3 was followed. Results for the TF was created by gathering translocation data from a wide spectrum of published literature. Search terms were mainly inputted into selected scientific databases in this format: Species name, "translocation index/factor" and the transition metal in question. For example, "Translocation factor, Sunflower, Cadmium" together. These terms are however imputed arbitrarily. The search generated varying amounts of hits depending on the species involved and the kind of metal in focus. However, some common exclusion criteria were used for all searches within this category. These include every output unrelated to heavy metals, articles where biological/chemical treatments were applied to improve plant growth or metal uptake and articles involving phytoextraction in water bodies. These exclusion criteria narrowed the articles to the amount present in the raw data section of the appendix page as depicted in the matrix cells. In some articles, the translocation values are described as 'translocation factors', in other ones, they are described as 'translocation index.'

The translocation data garnered were then entered as raw data in a spreadsheet format where every species in the matrix was cross referenced against every metal in focus and every individual data collected was imputed.

It is important to note that in some articles, the translocation data were already calculated, in some others however, the metal concentrations in the root and in the shoot were used to compute the translocation value for the species as they relate to a particular metal. Translocation factor/index value are computed by assessing the metal accumulation in both plant shoots and roots. This is expressed mathematically as follows (Zacchini et al., 2009):

$TF = \frac{C_s}{C_r} \times 100$ ……………………………………………………………Equation 3.1

where C_s and C_r represent metal concentration in plant shoots and roots respectively.

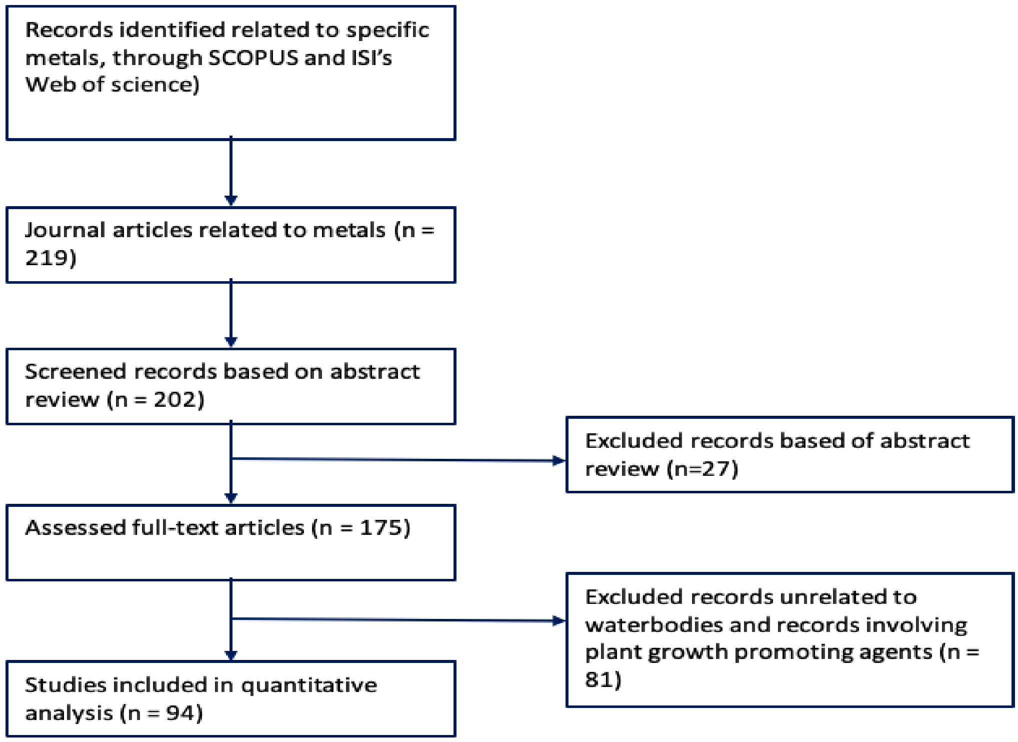


Figure 3. 3. PRISMA chart highlighting systematic review process for Translocation factor

3.2.4.2 Calorific value

The calorific value of any fuel describes the amount of heat energy derived from the complete combustion of a unit quantity of that fuel (Erol et al., 2010). To generate Calorific value data for the selected species, the systematic review protocol in Figure 3.2 was again followed. The Web of Science and Scopus databases were also used. For this category, the phrase "Calorific value" was imputed into the search bar in quotes followed by the species in focus. For example, *"Calorific value" Sunflower*. This was done for all the species in the matrix. This search yielded results in their hundreds for most of the species. However, when some exclusion criteria were applied, this reduced the results significantly to numbers where meaningful comparison can be made.

Exclusion criteria employed: Results were restricted to studies involving some form of green remediation technology. Also, calorific value considered were only for plant biomass (Straws), not oils or seeds. This is because post remediation interest is on plant biomass, and it should be the basis of any decision to be made.

3.2.4.3 Biochemical composition (% dry wt)

Plants cell walls are primarily made up of three organic compounds: cellulose, hemicellulose, and lignin. For bioenergy purposes, the desired kind of biomass is one with high lignocellulosic content (Isikgor and Bercer, 2015). For this study, comparisons were made on the lignocellulosic contents of the different plant species. These comparisons were made by collecting data from multiple articles, collate and average them to make comparison. The lignocellulosic contents of the plant species were measured from the dry matter of the biomass and expressed in percentages.

To collect data, the protocol as depicted by the review flow chart in Figure 3.2 was followed. The scientific databases Web of Science and SCOPUS were again employed, and different search terms were inputted into the search bar in different manners. Examples of search formats used are, search like: “Sunflower lignocellulosic content,” “Poplar biochemical composition,” “Cattail cellulose/lignin content.” Varying but similar percentage lignocellulosic contents were reported in different articles for the different species. To reduce the very large amount of hits that resulted from these searches, some exclusion criteria were set. These were collated and the mean values were computed.

3.2.4.4 Biomass production

Biomass production describes the quantity of a species biomass yield per unit area (in this case, tonnes per hectare) (Klass, 1998). This however should not be mistaken for species yield per unit area, as yield can sometimes be described in terms of fruits, seed or even oil yields. For this research, focus was solely on dry matter yields.

The systematic review protocol in Figure 3.2 was again employed. To obtain biomass production data for the different species in the matrix, the scientific databases, Web of Science and Scopus were used. This time, more diverse search terms were applied. Phrases such as “Sunflower biomass productivity”, “Soybean biomass yield”, “Poplar biomass production” etc. were imputed into the search databases. Again, this yielded varying degrees of hits depending on the species in question. Common exclusion standards were utilized for all species. For example, scenarios where biomass yield were modelled and not measured were excluded, review papers were not considered as source, articles where chemical and biological agents were used to improve production were excluded, hydroponics experiments were excluded (only field scale computations were considered), only dry matter yields were considered as well. Also, yield values expressed in tonnes per acre were converted to tonnes per hectare.

3.2.4.5 Root system

The maximum root depth of the different species was investigated and compared, and judgements were made on the plants with the deepest rooting system. Data for this category were mainly an adaptation from Canadell et al. (1996). In their study, they searched global maximum rooting depth data, spanning about 300 observations, covering over 250 woody and herbaceous species. Globally, species maximum rooting depth ranged from 0.3m to 68m. The study investigated rooting depth to species level detail. Maximum rooting depth of five of the eight study species were also recorded in the published database.

In a quest for more recent publications on species rooting depth, a thorough search on "maximum rooting depth" of these species was carried out on the Web of Science and SCOPUS databases, and no study captured as much detail as the one reported in Canadell et al. (1996). The closest was Schenk and Jackson (2002) but their investigations on rooting were more about vertical root profiles of different regions in space.

However, maximum rooting depth was investigated independently for the other three species in the matrix *(B. juncea, Miscanthus and Typha*). In the same manner, the databases were searched thoroughly following the review protocol demonstrated in the Figure 3.2 flow chart and the ones recording the highest root depth were recorded. These maximum depths were compared across all species. Root length measure was in metres.

3.2.4.6 Second generation attribute (SGA)

IEA Bioenergy (2009) defined first generation biofuels as biofuels that are readily available on the market. For example, biofuels from sugarcane, corn and pure plant oil. The feedstock from these biofuels in most cases are also useful as food or contains food residues. Second generation biofuels on the other hand are biofuels that are produced from cellulose, hemicellulose, and lignin. They are not grown primarily as food crops. Examples are bio-oil from pyrolysis or cellulosic ethanol. This category is important because sometimes plants bioenergy uses competes with their food uses. The aim therefore is to select plant species with the least competition with food uses. The basis for judgement was sourced from the Plant for a Future (PFAF) database, https://pfaf.org/user/Default.aspx (PFAF, 2019). The PFAF database is a compilation of over 7000 plant species, describing their most important characteristics, their edible and medicinal uses. This database is compiled from thousands of research articles been put together over a 10-year period. Plant species are assigned edibility ratings. A plant species' edibility rating describes how important the plant is as a food source. For this research, the higher the eligibility rating, the lesser its second-generation attribute. However, most of the species in the matrix are not primary food sources. The edibility ratings of the different species were compared, and their second-generation appeal were compared and ranked. This criterion however was not included in the matrix as this is an arbitrary subjective measure that is almost impossible to score quantitatively. The top performers from the MCDA analysis can be qualitatively accessed afterwards based on their second-generation attribute to ascertain the sustainability value in their usage for phytoremediation.

3.2.4.7 Crop growth rate (CGR)

A species' growth rate is defined as a measure of its increase in size, mass or quantity over a given time. As discussed earlier, there are several measures of growth rate in plant species but for this study, the crop growth rate (CGR) ($gm^{-2}d^{-1}$) will be used to estimate rate of change in plant mass per unit time. The growth parameter employed in the estimation is the dry weight as proposed by Hunt (1979) thus:

$$CGR = \frac{dw_2 - dw_1}{P \times (t_2 - t_1)} \quad \text{..Equation 3.2}$$

where dw_1 and dw_2 are dry weights taken at two separate times and t_1 and t_2 represents time 1 and time 2 respectively. P is the area of land used for planting.

The systematic review protocol in Figure 3.2 was followed to gather relevant information. Search terms used were in this manner; "crop growth rate" and name of species (usually both common name and scientific name), for example *"crop growth rate" sunflower* or *"crop* *growth rate" Miscanthus* as the case may be. Some exclusion criteria were set for this category. Articles using models to estimate CGR were excluded, hydroponic studies were excluded, and studies involving species stands younger than a year were excluded.

3.2.4.8 Yield Index (YI)

As stated previously, a species drought tolerance is described as its capacity to maintain productivity under drought conditions. This was described as Yield Index by (Gavuzzi et al., 1997). Expressed mathematically as:

$YI = \frac{Ys}{\bar{Y}s}$...Equation 3.3

where Y_s is the plant yield under stress and $\bar{Y}_s$ is the plant yield under optimal conditions. The higher the YI value, the greater its tolerance to drought conditions.

Productivity is usually defined in terms of yield. Plant yield on the other hand can be defined in terms of grain, oil, biomass, or seed yield but for the purpose of this study, focus is placed solely on biomass yield as the research objective is centred on generating sizeable biomass yield to be used as feedstock for a pyrolysis procedure. Study interest is on comparing the different species ability to produce optimum biomass yield under drought conditions. Drought here is determined by means of water potential.

A system's water potential tells us about the measure by which water molecules can move within it, as measured in Megapascal (MPa). Its maximum value is zero. As it moves towards the negative gradient, water potential reduces accordingly. Lower water potential therefore represents higher drought with the maximum water potential at zero.

To obtain data for drought tolerance index, the same protocol as shown in the review flowchart in Figure 3.2 was employed. The same scientific search databases employed for other criteria were used. Search terms used were *"drought tolerance", "drought resistance"* together with the plant species of choice. All data not using water potential as their means of measuring drought tolerance were eliminated from consideration. Data were aggregated, their means calculated, and comparisons were made. However, for the drought tolerance, it was difficult to make a fair comparison because species were not exposed to the same degree of drought. A simple ratio of productivity with drought/productivity without drought would not adequately give a fair account of drought tolerance if the level of drought is not considered. At this moment, no mathematical equation has been derived to factor varying levels of drought for even comparisons, this would be a limitation of the study at this point. However, judgements can be made by a qualitative assessment of plant productivity in the presence of different levels of water stress.

3.2.4.9 Metal Tolerance Index (MTI)

Tolerance index (TI) represents the relative growth rate of the plants and is equal to the growth in metal-containing solutions divided by the growth in control solutions, the quantity multiplied by 100. TI of fresh weight, dry weight or root length could be used to quantify plants metal tolerance (Wilkins, 1978). The higher the TI, the better the tolerance. However, because plants are exposed to different levels of metal contamination, to make an even comparison, it becomes necessary to adapt a modified metal tolerance index by introducing a concentration factor (CF) that reflects the phytotoxicity threshold of the metal in question, thus:

$$Modified\ MTI = \frac{Relative\ growth\ rate\ of\ metal}{Relative\ growth\ rate\ of\ control} \times CF \qquad \text{………………… .Equation 3.4}$$

Where $CF = Metal\ concentration\ used\ /\ Metal\ phytotoxicity\ threshold$

The results for metal tolerance were derived from the raw data by means of the formula above. These raw data were obtained by imputing search terms like *"metal tolerance"* "*heavy metal resistance"* together with the species of choice into the search databases.

3.2.5 Multicriteria decision matrix

This study utilizes data from a wide range of published literature, aggregate them to form an annex of information on whose basis decisions were made on suitable species for sustainably managing metal pollution.

Information from available published literature were also harnessed to determine a set of criteria and indicators suitable for benchmarking performances of selected phytoremediation species for transition metal control. Species suitability were measured differently for different criteria as was discussed in earlier sections.

Since data collected were from multiple sources and measured at different scales, it is important that these collated data be normalized using a standard normalization technique to bring all the data to a common scale for easier comparison. There are a number of normalization techniques in common use in the literature and some are summarized in Table 3.3 according to conditions of suitability.

Table 3. 3. Normalization techniques

Normalization method	Formulae	When to use	Literature
Multiples of median (MoM)	MoM (value) = Result (value) / Median (population)	Where results of individual tests are highly variable	Palomaki & Neveux, 2001
Min-max normalization	(value – min / max – min)	Where distribution is uniform across a fixed range	Kiran & Vasumathi, 2020
Decimal scaling	$v' = (v / 10^j)$ where j is the smallest integer such that $Max(\|v'\|)<1$	Where the distribution conforms to the power law	Patro & Sahu, 2015
Z-scores	Value – μ / SD	Where distribution has minimal extreme outliers	Cheadle et al., 2003

For this study, the performance measures in cells (see section 4.3.2) were derived by obtaining and collating corresponding data from the literature, then normalizing these data by calculating their min-max normalization values. Min-max normalization is a useful way of normalizing scores so that the best possible outcome for each criterion has a score of one and the worst outcome, a score of zero with every other value in between having a decimal score between zero and one. Min-max normalization (also referred to as feature scaling) seeks to perform a linear scaling of the raw data and tends to preserve the relationships among the raw data values (Kappal, 2019). The general formula is given in Table 3.3. Min-max normalized values were obtained by subtracting the minimum raw score of each criterion from each species' performance raw score for that criterion and dividing the result by the difference between maximum and minimum score for that criterion (See Table 4.10 footnote). Min-max normalization is advantageous in that assigned weights can be interpreted as 'importance' of the attribute (Liu, 2011). Essentially, each weight represents the significance of the attribute in relation to the overall utility scoring. In contrast, Z-score for instance implies that each assigned weight represents the effect of changing the outcome in an attribute by one standard deviation, which is more difficult to interpret (Liu, 2011). For this study, weights are to be assigned to criteria according to levels of importance making min-max normalization practicable. With regards to outliers, min-max normalization deals with this by replacing any outlier value lower than the minimum value with the minimum value and replaces any value higher than the maximum value with the maximum value (Kappal, 2019). In addition, for min-max normalization, the overall utility scoring of the transformed values is around the same scale which cannot be guaranteed with z-score normalization. This bounded range of normalized data will result in smaller standard deviation and consequently suppresses outlier effects. Preliminary MCDA matrix using z-score normalization showed an uneven distribution of scores with a wider range in differences (see appendix for z-score MCDA matrix).

The matrix uses the simple additive weighting (or weighted sum model) as described by (Tofallis, 2014). There are no expected problems of data dependency as highlighted by Pavlicic (2000) where the removal of a set of data for some candidates can alter the results and consequently ranking of other candidates.

The cells in Table 4.10 (in result section) contains the normalized value scores of the different species as it relates to the respective indicators investigated. These scores when put together and compared gives an indication of the suitability of species options. Criteria and their corresponding indicator can be weighted according to preferences of different individuals and stakeholders or according to clearly defined aims and objectives. For this study, priority weighting was given to growth rate, biomass production, metal accumulation and metal tolerance. Fast growth was considered crucial to this matrix because of the desire to attain maximum biomass production within the shortest possible time, as a major criticism of phytoremediation is that it takes a long time to attain remediation targets. Also, due to time constraints associated with planting season and the University calendar. Biomass production was also prioritised in the weighting as biomass is key to any bioenergy related project as the goal is to attain as much biomass as possible to be converted via a thermochemical treatment to gain valuable bioenergy and usable by-products. Metal accumulation and tolerance is given priority also because the overarching aim of the research is to extract metal contaminants from contaminated sites using accumulator plants.

3.3 Methodology for Phytoremediation study

As depicted in the flow chart in figure 3.1, the top performer in the MCDA was used as a model plant to carry out a phytoremediation study.

3.3.1 Soil properties

3.3.1.1 Soil pH

Soil pH was determined by using a calibrated glass pH electrode probe. Sieved soil samples were measured (10 g) and put into a clean beaker, 10ml of deionised water was added to it. Stirring of the mixture was carried out using a sterilized glass rod and left to stand for 30 minutes. Afterwards, the calibrated pH electrode probe was placed in the mixture suspension and the pH reading was taken. This was replicated three times for certainty.

3.3.1.2 Soil texture

Standard 'feel' test as described by Thien (1979) was used to determine the texture of the soil. Prior to test, drops of distilled water were added to soil to form individual balls till appropriate for test.

3.3.1.3 Soil moisture content (SMC)

To determine moisture content, 10g of soil was placed in a muffle furnace and heated at 105°C for 24 hours, afterwards cooled in a desiccator and weighed. Soil moisture content was computed thus: SMC = $\frac{Initial\ weight - final\ weight}{final\ weight}\ X\ 100$ ………………….Equation 3.5

3.3.1.4 Soil organic matter (SOM)

Samples used to determine SMC were further heated at 450°C for 6 hours till sample becomes ash completely, then allowed to cool in desiccators, then weighed. SOM was determined thus:

$\%SOM = \frac{Initial\ weight - final\ weight}{final\ weight}\ X\ 100$……………………………………….Equation 3.6

3.3.1.5 Cation exchange capacity (CEC)

To determine soil CEC, standard method as described by USEPA method 9081 (USEPA, 1986) was adopted. Air dried soil (5g) was weighed and put in 50ml centrifuge tubes, then 30ml (1M) of sodium acetate was added to the tubes. These were placed in ultrasonic bath and agitated for 10 minutes then samples were centrifuged for 5 minutes at 3000 x g. The resulting supernatant was then decanted. Afterwards, 30ml of ethanol was added to the tube, shaken, centrifuged again and then decanted. This was repeated to ensure elimination of excess sodium acetate. The resultant soil sample was extracted using 20ml (1M) of ammonium acetate following the protocol as described earlier. This was replicated thrice, then the resultant supernatant was filtered, collected in a volumetric flask, and filled with distilled water up to the 100ml mark. To determine cation concentrations, an already calibrated inductive coupled plasma optical emission (ICP-OES) was used.

Data analysis and computations:

$$Sample\ concentration = \frac{\left\{\frac{C\ x\ D\ x\ V}{S}\right\}}{R}$$ ……………………..Equation 3.7

Where:

C= Concentration from extract (ppm or mg/L)

D= Dilution factor

V= Volume of extractant

S= Dry weight of soil sample (mg)

R= Relative atomic mass of element (Na- 22.99, Mg= 24.3, K= 39.1

$$Cation\ exchange\ capacity \left(\frac{\mathrm{cmolcKg}}{\mathrm{L}}\right) = \mathrm{Na + Mg + K + Ca}$$ ……………………Equation 3.8

3.3.2 Enumeration of soil microorganisms

To determine soil microorganism numbers, plate count method was employed. Soil sample (1g) was weighed and added to 9ml of deionized water, shaken and covered in a plastic bottle to make up 10^{-1} dilution. One ml of the soil solution was taken out of the bottle and transferred to another bottle of 9ml distilled water to form the 10^{-2} dilution. This process was repeated to get through to 10^{-7} dilution. Aseptic techniques were then used to transfer 1ml of solution to petri dishes containing approximately 20ml appropriate molten agar, inverted and incubated at 25°C for 4 days. Glycerol Yeast Extract Agar (GYEA) was used for actinomycetes, Tryptic Soya Agar (TSA) was used for bacteria and Sabouraud Dextrose Agar (SDA) was used for fungi.

3.3.3 Heavy metals determination

To determine total metal concentration, the EPA 3051a protocol (USEPA, 2007a) was followed. 0.5g of air-dried soil sample was weighed and put in a Teflon tube, then 9ml of nitric acid (HNO_3) and 3ml of hydrochloric acid (HCl) were added to tube. This was then placed in a closed microwave oven (CEM, Model Mars Xpress). Samples were kept in this closed system for 10 minutes at 175°C in accordance with the method protocol, then left to cool before being centrifuged at 3000 x g for 5 minutes. Afterwards samples were filtered into a 50ml volumetric flask using Whatman's No 42, then filled to the 50ml mark using distilled water. Samples were safely kept in fridge at 4°C in preparation for analysis.

To take triplicate readings for soil sample extract and a blank sample, a Thermos ICP-OES (iCAP 6000) was used. Calibration of the instrument was carried out using a mixed metal standard solution having concentrations ranging from 0.1 mg/kg to 10 mg/kg. Glassware and plastics used were treated using dilute (1:1) nitric acid for 24 h and rinsed with MilliQ water prior to use. Quality control measures taken are the analysis of loam soil certified reference material CRM (SQC001-050G (lot 011233)) and the use of laboratory reagent blanks. Recovery percentage of metal concentrations based on CRM ranged from 92.1 to 108.45%.

3.3.4 Preparation of *Bacillus aryabhattai* AB211

B. aryabhattai AB211 was isolated and kindly provided by C. Bhattacharyya (Bose Institute, India). It is used to investigate plant growth and phytoremediation promoting potential together with *H. annuus* seedlings in pot trials. Seeds of *H. annuus* were sown in pots containing 1kg of sieved soils each as the other treatments described in section 3.3.1 *B. aryabhattai* AB211 culture was grown in M9 minimal media for 72 hours to attain about 10^8 cfu/ml. After plant germination, the rhizospheres of 10-day-old seedlings were inoculated with the isolate (inoculation with about 10^8 cfu/ml of AB211 culture; and in soil) at a ratio of

10ml to 100g of soil. 100ml of bacteria medium was used per pot. Initial metal concentration was kept at figures shown in Table 3.4

3.3.5 Soil and metal stock preparations

Air dried sieved loam soils were obtained from Kettering Soil Limited (UK). Approximately 30 kg of soil were weighed to be put in 30 pots. Based on general plant toxicity thresholds of Pb, Cd and Zn which is reported as 120, 32 and 160 mg/kg respectively by EPA (2007), the current study aims to keep initial concentrations at 300, 50 and 600 mg/kg for Pb, Cd and Zn respectively. These concentration levels represent upper critical soil concentration levels for plants (Kabata & Pendias, 1984). Analytical grade of lead nitrate [$Pb(NO_3)_2$], zinc chloride ($ZnCl_2$) and cadmium chloride ($CdCl_2$) were dissolved separately in a litre of deionized water to make stock solutions (with expected concentrations at 50 mg/kg, 300 mg/kg and 600 mg/kg for Cd, Pb and Zn, respectively) for the different metal salts. Total soil quantity required for experiment was 30 kg, i.e., 3 kg of soil per treatment which equates to 1 kg of soil per pot as shown in Table 3.4. To attain 50 mg/kg of Cd in 3 kg of soil, 0.245g of $CdCl_2$ was dissolved in 1 L of distilled water by stirring continuously until metal is completely dissolved in water, then mixed with 3kg of soil to spike in a 10 kg/L ratio. To attain 300 mg/kg of Pb in 3 kg of soil, 1.44g of $Pb(NO_3)_2$ was dissolved in water and mixed with soil. For Zn, 3.774 g of $ZnCl_2$ was required to attain 600mg/kg of Zn in 3kg of soil as shown in Table 3.4.

3.3.6 Experimental protocol

The experiment uses a completely randomized design involving three metal types, Cd, Pb and Zn with *H. annuus* the plant being the subject of experimentation. Plant choice is based on the outcome of the MCDA study in chapter 4. All *H. annuus* seeds were obtained from Mr. Fothergill's seeds, Kentford. The different treatments enumerated in Table 3.4 were applied to *H. annuus*. All 30 pots were filled with 1kg mass of soil each. Ten seeds of *H. annuus* was sown on each pot. Soil was irrigated regularly to keep at field capacity ideal for plant growth. At week 10, plant samples were harvested and separated into roots, stems, and leaves, then oven dried in the laboratory at 65 $\pm 2°C$ for 72 hours. Roots were rinsed in warm deionized water to remove every soil debris present. Important data (dry weight, bioconcentration factor, translocation index, metal tolerance index) investigated with the matrix were measured empirically using standard methods.

Table 3. 4 Phytoextraction experimental design summary

Treatments	Replicates	Soil quantity	Weight of metal salt required (g)	Target metal conc.
Cd	3	1kg x 3 = 3kg	0.245g of $CdCl_2$	50mg/kg
Pb	3	1kg x 3 = 3kg	1.44g of $Pb(NO_3)_2$	300mg/kg
Zn	3	1kg x 3 = 3kg	3.774g of $ZnCl_2$	600mg/kg
Cd+Pb+Zn	3	1kg x 3 = 3kg	$CdCl_2$ (0.245g) + $Pb(NO_3)_2$ (1.44g) + $ZnCl_2$ (3.774g)	Sum of all 3
Control	3	1kg x 3 = 3kg	Blank	Blank
AB211	3	1kg x 3 = 3kg	Blank	Blank
Cd + AB211	3	1kg x 3 = 3kg	0.245g of $CdCl_2$	50mg/kg
Pb + AB211	3	1kg x 3 = 3kg	1.44g of $Pb(NO_3)_2$	300mg/kg
Zn + AB211	3	1kg x 3 = 3kg	3.774g of $ZnCl_2$	600mg/kg
Cd+Pb+Zn+AB211	3	1kg x 3 = 3kg	$CdCl_2$ (0.245g) + $Pb(NO_3)_2$ (1.44g) + $ZnCl_2$ (3.774g	Sum of all 3
Total	**30 pots**	**30 kg**		

3.3.7 Calculating important parameters

3.3.7.1 Bioconcentration factor (BCF)

The BCF is defined as the ratio of metal concentration in the plant to the metal concentration in the soil (Zhuang et al., 2007). It is defined mathematically as:

$$\text{BCF} = \frac{Metal\ concentration\ in\ plant\ tissues\ (mg\ kg\ \ DW)}{Metal\ concentration\ in\ soil\ (mg\ kg\ DW)} \text{..Equation 3.9}$$

For plants, BCF values above 1 are generally referred to as hyperaccumulators (Zhang et al., 2002).

3.3.7.2 Translocation factor (TF)

This is used to ascertain the ability of plants to translocate metals from its roots to the above ground harvestable shoots (Nirola et al., 2015). It is calculated mathematically thus:

$$TF = \frac{Metal\ content\ in\ aboveground\ shoots}{Metal\ content\ in\ rots}\ x\ 100 \text{..Equation 3.10}$$

3.3.7.3 Metal tolerance index (MTI)

This is defined as the mean weight of plants exposed to heavy metal stress divided by the mean weight of the control (Baker at al., 1994).

$$MTI = \frac{Dry\ weight\ of\ metal\ plants}{Dry\ weight\ of\ control}\ X\ 100 \quad \text{.................Equation 3.11}$$

3.3.8 Statistical analysis

The statistical tests used are the Analysis of variance (ANOVA) and Tukey's post-hoc test to compare treatments. This is because comparisons were made for more than two data sets (multiple treatments) with a single dependent variable (e.g., % dry weight) at a time. Tests were used to compare biomass production, metal tolerance and accumulation efficiency of sunflower when exposed to different metal treatments and to compare metal accumulation efficiency of sunflower with and without the bacterial strain *B. aryabhattai* AB211. All statistical analyses were carried out using the Minitab version 17 software. Means/median differences were deemed statistically significant at $p \leq 0.05$. All experiments were subjected to normality and equal variance assumption tests.

3.4 Methodology for pyrolysis study

3.4.1 Measuring the calorific value of biomass sample prior to pyrolysis

The calorific values of the plant biomass samples were measure via calorimetry. This involves the total combustion of a known quantity of biomass sample inside an oxygen bomb calorimeter under carefully controlled conditions (Hunce et al., 2019). To determine the calorific value, 0.5 g of dry biomass sample was squashed and put into the bomb calorimeter (IKA, C6000), and this was filled with excess oxygen under pressure to ensure total combustion. The calorimetric bomb was then immersed in a container filled with water (2150 ml), with the initial temperature of the water at 18 ± 0.5 °C. The water bath temperature was measured with a temperature probe at 10s intervals. The temperature variations during combustion were used to work out the quantity of heat energy released. Results of this process were expressed in MJ per kg.

3.4.2 Estimating pyrolysis product

The sunflower biomass derived from the phytoremediation study in chapter five was prepared for use in the pyrolysis study. Biomass for the three different metal treatments (Cd, Pb, Zn) were homogenized to get adequate quantity for pyrolysis. Homogenized samples were washed with deionized water to remove debris, then air-dried. Total heavy metal content of homogenized biomass samples was measured using the USEPA 3051a protocol described in section 3.3.3.

Biochar was produced through pyrolysis of dried sunflower biomass under oxygen limited conditions. Shredded (<5cm) dried biomass samples were sent to BEACON Biorefining Centre of Excellence, University of Aberystwyth and pyrolysis was undertaken using a small-scale benchtop tube furnace (see figure 3.2). Biomass was slowly pyrolyzed at 500 °C with a 2-hr residence time in a N_2 environment and heating rate of 10°C/min, recognized as process parameter conditions for optimum biochar yield production (Granados et al., 2022).

Biochar yield was estimated thus:

$$Biochar\ yield\ (\%) = \frac{Weight\ of\ biochar}{Dry\ weight\ of\ biomass}\ x\ 100 \text{..................................Equation 3.12}$$

Bio-oil yield data was obtained based on adaptation from Tang et al. (2020) where machine learning tools were used to estimate the bio-oil yield based on the feedstock type and pyrolysis parameters. This was done because due to the size of biomass obtained from the phytoremediation process (120g), pyrolysis needed to be done using a bench scale tube furnace (see Figure 3.4) designed primarily for char production. In the same vein, syngas data was derived based on simulation using a computer-based model Aspen Plus V9 given the process parameters enumerated above.

Figure 3. 4. Bench scale tube furnace at BEACON Biorefining Centre

3.5 Methodology for Column experiments for wastewater treatments.

3.5.1 Material preparation and characterization

Biochar samples when received were grounded with agate mortar to achieve homogenization and sieved to 0.5 – 1 mm sized particles. This was washed with deionized water to remove impurities and resident ash debris and then dried at 80 °C to prepare for further analysis. Stock solutions of 50 mg/L, $CdCl_2$, 100 mg/L $Pb(NO_3)_2$, 150 mg/L of $ZnCl_2$ were prepared by dissolving the appropriate amount of metal salt in deionized water.

Biochar pH was determined by adding biochar to deionized water in a 1:20 mass ratio, then stirred and allowed to stand for 10 minutes before taking pH reading using a pH meter (Inyang et al., 2012). See 3.3.4.1. Total heavy metal content of the pre- and post-sorption biochar was measured using the USEPA 3051a protocol described in section 3.3.6.

Heavy metal content of the post-sorption leachate was measured following the EPA 3015a protocol (USEPA, 2007b). 22.5 ml of metal contaminated aqueous solution was sampled out in Teflon tube and 2.5 ml of concentrated nitric acid was added to meet the 9:1 ratio between sample volume and nitric acid volume as recommended by the EPA 3015a method. Samples were mineralized in closed microwave oven (CEM, Model Mars Xpress) and the procedure described in 3.3.6 was followed afterwards.

To determine the speciation of metal in post-sorption biochar, a sequential extraction procedure was carried out following a four-step process adopted from von Gunten et al. (2017).

Step 1: Acid extractable fraction (F1): 0.5g of dried biochar sample was weighed in an analytical weighing scale and put in a 50 ml centrifuge tube. 20 ml of 0.1M acetic acid was added to biochar sample and shaken in a rotational shaker for about 16 hrs then centrifuged for 15 minutes at 10,000 relative centrifugal force (rcf). 10 ml of the supernatant was collected carefully using a syringe and was filtered using 0.2 μm nylon membranes. Extreme care was taken because of the light and buoyant nature of floating biochar particles on the surface of the supernatant after centrifugation. Residual liquid and solid samples were flushed using ultrapure water via a vacuum filtration system using 0.2 μm nylon membranes to retrieve the remaining solids. These solids were then transferred back to tubes (aided by dispersal using ultrapure water) and oven-dried at 60°C

Step 2: Reducible fraction (F2): Residual oven-dried solids were extracted further following steps as described above but with 20ml of 0.1M hydroxylamine chloride ($NH_2OH{\cdot}HCl$) (previously adjusted to pH 2 using nitric acid). Liquid from extraction were recovered via centrifugation and solids were washed as described above.

Step 3: Oxidizable fraction (F3): 5 ml of 30% H_2O_2 was added to sample and was allowed to stand for an hour at room temperature then another 5 ml of 30% H_2O_2 was added to tubes then heated on a heating block for anther hour. Afterwards, 25 ml of 1M ammonium acetate (previously adjusted to pH 2 using nitric acid) was added and the solution was mixed for approximately 30 minutes. Sample was centrifuged again, supernatants recovered, and samples were washed again as has been described above for the final extraction step.

Step 4: Residual fraction (F4): The leftover biochar was put into ceramic trays and burned in furnace for 6 hrs at 500°C. Residual ash was then transferred to Teflon tube for acid digestion. Extreme care was taken when transferring ash from ceramic trays not to lose solid mass. Digestion was carried out following USEPA 3051a protocol as described earlier in 3.3.6. The procedure was carried out in triplicates.

3.5.2 Column leaching experiment

A column leaching experiment was carried out with plastic column (15 cm height, 3.5 cm inner diameter) to investigate the effect of sunflower-derived metal-enriched biochar on the removal of metal contaminants from aqueous solution. Initially, nylon membrane filter (0.2μm) was placed at the bottom of the column to prevent adsorbent loss during experiment. Membrane filters were used as these does not adsorb metal ions as has been reported for Whatman's filter paper (Engin et al., 2010). Afterwards, a 2 cm of fine gravel (5mm) and a known mass of biochar (10cm) was packed into the column, then another 2 cm layer of fine gravel was placed on top of the biochar layer to block materials into column. Prior to the start of experiment, the column was run in a downward stream with deionized water to saturation to get rid of any trapped air between particles (Lim & Aris, 2014). The top of the column was pierced with a sterile Intrafix 150 cm infusion set (BBraun) then connected to a peristaltic pump which was used to set and maintain flow rates adopted in the procedure. See Figure 3.5 for column schematics. The duration of the experiment was 38 hr at which point leachate was taken with an approximate flow rate of 0.22 ml/min. Leachate samples were further filtered using nylon membrane filters (0.2 μm). Post-sorption biochar was washed with deionized water and dried for analysis. Filtrate was acidified with concentrated (65%) nitric acid to pH $\leq$ 2 and stored at 4 °C for analysis. Cd, Pb and Zn concentrations of the acidified filtrate samples were analysed using USEPA 3015a digestion method described in section 3.5.1, followed by an ICP-OES analysis.

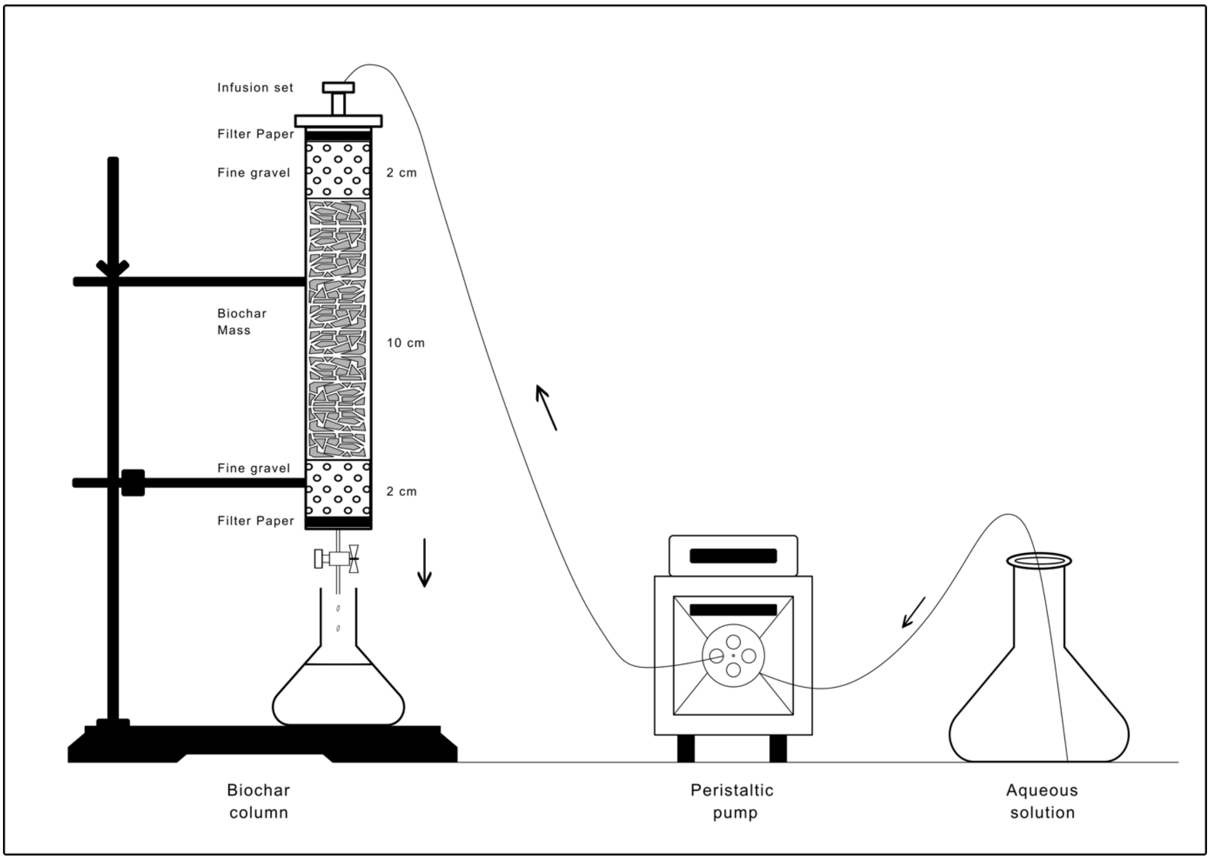


Figure 3. 5. Schematics of column experiment

3.5.3 Batch adsorption isotherm experiment

Metal-rich biochar samples from pyrolysis experiment was used to carry out a multi-metal batch adsorption isotherm experiment to further investigate heavy metal removal efficiency and to understand the adsorption behaviours of metal ions (Cd^{2+}, Pb^{2+}, and Zn^{2+}) from heavy metal contaminated water. The experiments were carried out in room temperature 21 ± 2 °C and in triplicates. 0.2 g biochar (adsorbent) was added to a 200 ml conical flask containing a 100 ml of metal (Cd^{2+}, Pb^{2+}, and Zn^{2+}) solutions. The metal concentrations were set from 10 mg/L to 200 mg/L. The concentrations were set following procedures described in 3.5.2. Initial pH of metal solutions was set at 5 by adjusting with nitric acid and sodium hydroxide. This was set so to keep metal ions stable in the solution without precipitation (Ding et al., 2016). The mixture in flask was placed in a rotary shaker and shaken for 24 h to ensure adequate adsorption/desorption. Heavy metal concentrations in the supernatant were measured via ICP-OES

3.5.4 Statistical analysis

As with section 3.3.8, the statistical tests used are also the Analysis of variance (ANOVA) and Tukey's post-hoc test to compare treatments. Tests were used to compare the capacity of metal-enriched sunflower-derived biochar to remove metal contaminants from wastewater under different heavy metal treatments. Also, the statistical analyses were carried out using the Minitab version 17 software. Means/median differences were deemed statistically significant at $p \leq 0.05$.

CHAPTER FOUR

DEVELOPING A MULTI-CRITERIA DECISION MATRIX FOR SPECIES SELECTION

4.1 Background

As mentioned in section 1.1 of this report, this study seeks to explore the applicability of phytoremediation as a medium to manage toxic metal contamination in soils. To maximize benefits from a phytoremediation process, Pandey et al. (2016) proposed combining phytoextraction with an energy generation process. Generating energy from the phytoremediation process by utilizing energy crops for metal extraction can be a useful way of gaining added value from the process (e.g., Tripathi et al., 2016; Raikova et al., 2019; Rheay et al., 2021; Wang et al., 2021). The first stage in the process is a bio-extraction function which involves utilizing plants to extract metal contaminants from the soil. Its effectiveness depends greatly on the bioaccumulation potential of the species, growth rate and yield generation attributes (Tangahu et al., 2011). The efficiency of the bioenergy generation process also depends on the species' lignocellulosic properties, biofuel properties and calorific value (Pandey et al., 2016). Additional efficiency parameters for both processes are species' tolerance to diverse kinds of abiotic stresses, cost, and second-generation attribute (Tripathi et al., 2016). For the success of these combined processes, the types of species selected is crucial. Species selected should possess a significant number of these attributes. To achieve the desired outcomes in this regard, identifying and selecting the best plant species is critical. The process of selecting plant species must consider all the underlying suitability criteria for the plant species and determine the most suitable fit. A multicriteria decision analysis (MCDA) tool may satisfy this requirement. It provides a platform to evaluate all the complex suitability criteria for different plant species in a comprehensive and verifiable manner and allows for informed decision making given the outcomes of the assessments.

The goal of decision makers is always to choose the optimal option. In reality however, true optimal decisions usually only exist where there is a single criterion for consideration. Unfortunately, most world problems come with multiple complex and conflicting criteria on which basis decisions are to be made. Where there are multiple criteria, a framework for breaking down these complexities into smaller components for better assimilation becomes necessary. A multi-criteria decision analysis (MCDA) seeks to structure and solve decision making problems involving multiple defining criteria. Ultimately, its aim is to make decision making easier. It is a useful tool for breaking complex decision-making problems into smaller components, weighing, analyzing smaller pieces, and making judgements, then reconstructing back to a whole to paint a vivid picture for a more informed decision making.

In a published scoping study on environmental appraisal techniques and guidance by the UK Department of the Environment, Transport and the Regions (DETR, 1999), a major recommendation for future action was a continuous provisioning of guidance for the development of multi-criteria analysis framework. This popular tool essentially combines a range of options for a designated objective(s), gather and synthesize information for these options, make comparisons, trade-offs, etc. to arrive at a comprehensive easy-to-assimilate framework for decision makers. The multi-criteria analysis tool has been employed in recent times to handle decision-making problems relating to the environment, energy and sustainability (Zavadskas et al., 2015; Soltani et al., 2015), tourism (Akincilar and Dagdeviren, 2014), information technology and manufacturing (Oztaysi, 2014), supply chain and logistics (Rajesh and Ravi, 2015), construction and project management (Monghasemi et al., 2015), amongst others.

A few studies (e.g., Rheay et al., 2021; Wang et al., 2021; Raikova et al., 2019 Jiang et al., 2015; Tripathi et al., 2016) have evaluated specific bioenergy crops (based on hyperaccumulation and biofuel potentials) as candidates for a synergistic association with phytoremediation. However, there is a lack of across-board analytical review, involving multiple species, as well as considering multiple suitability criteria to determine suitable candidates for a synergistic approach to metal pollution clean-up. Developing a more robust selection process would vastly improve our understanding of comparative plant species behaviour under different conditions and exposures. In addition, the outcome is more reliable as the candidates have been exposed to more suitability checks.

Managing environmental contamination issues requires a plethora of decision-making. To make these kinds of decisions, a range of factors such as project objective, stakeholder inputs, scientific findings etc. are often considered. To determine the species best suited to attain the synergistic goal of phytoremediation and bioenergy generation, it is necessary to develop a selection mechanism that considers the aforementioned set of criteria. An MCDA approach appears to be a suitable mechanism to attain this goal. It is an approach that helps synthesize available information, compare different objectives and technologies, make necessary trade-offs to arrive at a coherent, integrative resolution.

4.2 Aim and objectives

This part of the study aims to recognize the complex nature of decision making as it relates to desired outcomes of multiple stakeholders and develop a multi-criteria analysis matrix based on a set of established criteria to determine which phytoremediation species is (are) best suited for the purpose of phytoremediation and bioenergy generation.

Some objectives set to achieving this aim are:

- To identify suitable plant species and relevant suitability criteria for a phytoremediation and bioenergy-generation synergy.
- To identify the key performance index for set criteria and gather relevant data from available scientific databases.
- To develop a multicriteria matrix based off quantitative data collected from studies published in these scientific databases.
- To assign weights based on criteria priority ratings and make decisions according to established research objectives.

4.3 Results and discussion

Results were gathered from over 190 journal articles reviewed (See section 3.2.4). Data were collected for the different categories of plants, their designated criteria and corresponding key performance indicators (in brackets) the analysed and the means calculated for simple performance comparison, and these were ranked. Mean values were calculated by summing performance data of the species investigated (from selected articles) and divide by the total number of observed data in selected articles (for each criterion) (see raw data in appendix for articles).

Mean = $\frac{Sum\ of\ all\ the\ observations}{Total\ number\ of\ observations}$ ....Equation 4.1

Species are ranked based on performance scores for every criterion investigated and the difference in performance scores need not be statistically significant to be ranked higher or lower. Rankings are necessitated as part of the model development procedure and its design expectation is for it fit well even when applied to different species under different objectives or priorities. Rankings gives an indication of performance prior to the application of weights (based on stakeholder priorities).

On data quality, the Yield Index is the KPI with the least reliability as already highlighted in 3.2.4.8. While yield index is a good measure of drought tolerance for specific case studies (Anwar et al., 2011), there is implicit difficulty to make a fair comparison when species were not exposed to the same degree of drought. Because difference in drought exposure levels will have a profound effect on species' drought tolerance capacity, the greatest uncertainty of the matrix lies here. Tolerance data may skew in favour of conditions where drought level is low. To manage this, tolerance data from the literature were collected from conditions with similar drought exposure levels. This was included as part of the exclusion criteria for drought tolerance data. However, this significantly reduced the number of studies evaluated and thus the robustness. For this study, it may be ascribed to poor data quality due to the unavailability of more input data which means a better formula for aggregating more diverse drought tolerance level is needed or more input data are needed rather than the approach being not well founded.

4.3.1 Species performance according to specified Criteria/KPIs

4.3.1.1 Pollutant accumulation (translocation factor)

After obtaining multiple raw data on the translocation values from different studies as indicated in PRISMA chart in Figure 3.3, the translocation data for different species with respect to the metals were then collated and aggregated and then the mean was calculated to get a single mean translocation factor value for each species and metal, and these were structured in a matrix to make for easy comparison. Comparisons were made and species were ranked based on average performances accordingly. Results in Table 4.1 showed that soybean had the best performance based on mean translocation factor, followed by poplar, Indian mustard, and sunflower. Comparatively, cattails and switchgrass were the least performing plant species with the lowest averages on metal accumulation percentages. The TF values in the literature are very varied and are influenced by a myriad of factors such as, environmental factors, metal bioavailability, metal type and concentration (Nirola et al., 2015). The values given are an aggregation of data exposed to different sets of factors that may have influenced uptake levels in different ways. Derived data should be regarded as merely indicative as factors affecting results are largely unknown for aggregated data and it is important that translocation data be sourced according to conditions that fit desired objective.

Generally, TF values > 1 are regarded as hyperaccumulators. However, where the level of metal concentration is low, this condition is easier to meet than in heavily polluted conditions like an abandoned mine soil. Baker & Brooks (1989) opined that those plants accumulating >1000 mg kg^{-1} of Co, Cr, Cu, Pb and 10,000 mg kg^{-1} of Zn or Mn are referred to as hyperaccumulators, implying that TF values are more qualitative rather than quantitative. Ideally, phytoremediation projects should factor in quantitative considerations as well the qualitative ones when seeking the ideal species. However, there is lack of universally established metal concentration thresholds for all heavy metals to base the 'hyperaccumulator' status on, therefore the qualitative aspect remains the most common in the literature. While the ideal TF value for species hyperaccumulation should > 1, species with TF values < 1 can still be ideal for phytostabilization (Yoon et al., 2006).

Table 4. 1. Mean translocation factor for the different species

Species	Mean translocation factor					
	Cd	Cr	Cu	Ni	Pb	Zn
Sunflower	83.83	7	64.22	69.07	55.43	103.15
Indian mustard	65	68.25	77.3	48.73	75.53	72.2
Soybean	56.3	43.5	147.4	24	146	125
Silvergrass	41.5	89	37.65	55.15	28	49.73
Poplar	129	19.3	71.9	38.1	28.25	121.65
Willow	12.5	17.63	28.15	35.8	11.8	154
Switch grass	19.95	37	52	12	18.23	28
Cattails	12	25	20.75	27.5	9	35

See Appendix for complete raw data showing range around the means presented here.

4.3.1.2 Calorific value

On applying specified exclusion criteria, results showed species' multiple calorific values from different studies. These values were aggregated, and their means were computed to get a single value for each species from which comparisons were made and calorific values were ranked from highest to lowest. The calorific value in the results section is expressed in Mega Joules per Kilogram (MJ Kg^{-1}). As shown in Table 4.2, the calorific value for the different species shows marked similarity even though it appears poplar and willow are the best performers with soybean and switchgrass being the least performers. Calorific value data ranged from 17.25 to 20.46 MJ Kg^{-1}. The difference in mean calorific values between silvergrass, sunflower and Indian mustard appears very miniscule on aggregation, but the overall range of the raw data was more varied. However, the range is consistent with calorific values of fast-growing grasses and forbs (Demirbas, 2002; Llorente et al., 2006, Sannigrahi et al., 2010). Even though the difference in calorific value is not significant, ranking was still carried out as part of the model development and testing, and data could potentially differ more significantly with different species. The calorific values recorded represents a range deemed ideal for potential bioenergy crops (Dominguez et al., 2017). These values are however lower than the calorific value for alternatives like coal (22.7 MJ Kg^{-1}) (Boundy et al., 2011) but are within the range of forest shrubs and trees that are generally good indication of adequate heating energy potential (Boundy et al., 2011). Saidur et al. (2011) also reported that the heating value of species correlates well the lignin content of the lignocellulosic biomass. Higher lignin content in plants usually means higher heating value which makes lignin an important constituent of plants' biochemical composition.

Table 4. 2. Mean calorific value of the different species

Species	Calorific value	Rank	Selected references (See Appendix for full reference list)
Sunflower	18.81	4	Demirbaş, A., 2002; Werther et al., 2000; Magasiner, N. and de Kock, J.W., 1987
Indian mustard	18.80	5	Maiti et al., 2007; Llorente et al., 2006; Werther et al., 2000.
Soybean	17.25	8	Werther et al., 2000; Şensöz, & Kaynar, İ., 2006
Silvergrass	18.84	3	Sannigrahi et al., 2010; Wilén et al., 1996; Illerup & Rathmann, 1997; Hallgren et al., 1999.
Poplar	20.46	1	Blunk et al., 2000; Kitani & Hall, 1989; Gaur & Reed, 2020
Willow	19.77	2	Aylott et al., 2008; Miller, R.S. and Bellan, J., 1997
Switch grass	17.40	7	Miles et al., 1995; Agblevor et al., 1997
Cattails	18.58	6	Dubbe et al., 1988.

4.3.1.3 Biochemical composition (% dry wt)

These were collated and the mean values were computed. To determine the species with the higher lignocellulosic content, emphasis was placed on the different organic polymers in this order: lignin, cellulose, and hemicellulose. Species with a higher lignin/cellulose ratio are generally considered more lignocellulosic. These species were then ranked from 1-8 on best to worst lignocellulosic content and detailed alongside their respective references as shown in Table 4.3. To rank, lignocellulosic data were weighted in this ratio: Lignin (50%), cellulose (30%) and hemicellulose (20%). Lignin is given priority because higher lignin content usually correlates with higher heating value (Saidur et al., 2011). Woody species (which typically have higher lignin content) have higher calorific value than herbs and straws (Amezcua-Allieri & Aburto, 2018). Biomass with high cellulose content is also important because bio-oils are mainly derived from them (Jahirul et al., 2012). Poplar and willow were the best performers as these are woody plants with high lignocellulosic potentials. Indian mustard and switchgrass performed the least on this criterion.

Table 4. 3. Mean lignocellulosic content of the different plant species from published data

Species	Cellulose	Hemicellulose	Lignin	Weighted score	Rank	Selected references (See Appendix for full reference list)
Sunflower	41.47	29.33	20.33	24.84	3	Salasinska et al., 2016; Demirbaş, A., 2002
Indian mustard	40.15	26.28	7.6	10.84	8	Maiti et al., 2007; Simbaya et al., 1995
Soybean	49.83	18.83	8.67	15.43	7	Reddy & Yang, 2009; Weizheng et al., 2014
Silvergrass	51.58	23.82	13.86	21.77	4	Brosse, 2012; Leemhuis, & de Jong, 1997
Poplar	46.4	21.63	24.38	25.84	2	Sannigrahi et al., 2010; Leemhuis, & de Jong, 1997
Willow	51.34	24.36	21.21	27.31	1	Szczukowski, 2002; Leemhuis, & de Jong, 1997
Switch grass	38.35	33.58	7.8	17.26	6	Howard et al., 2003; Lemus et al., 2002.
Cattails	47.58	21.2	12.4	17.92	5	Elhaak, 2015; Vetayasuporn, 2007

4.3.1.4 Biomass production

All the yield values from the different articles were collated and their means were calculated to give a single mean yield value per species. This was done so that meaningful comparisons can be made. Species were ranked according to average performance and the respective references were also captured. For a synergistic phytoremediation/bioenergy project to be successful, biomass yield of the species should be ideally high. The more the biomass production, the higher the volume of feedstock for valorization. Also, higher biomass production is also essential for higher metal accumulation (Jiang et al., 2015). As shown by their mean yield values highlighted in Table 4.4, sunflower had the best performance, then silvergrass and cattails. These herbaceous species are especially advantageous for their high biomass yield (which can get over 20 t DW ha-1 yr-) (Rabêlo et al., 2018), which can then be harvested and used as a bioenergy source (Balsamo et al., 2015), in addition to their usefulness as phytoremediation plants.

Table 4. 4. Mean biomass yield of the different species

Species	Biomass production (Tons/ha)	Rank	Selected references (See Appendix for full reference list)
Sunflower	16.40	1	Ion et al., 2014; Ibrahim, 2012
Indian mustard	9.65	6	Maiti et al., 2007; Blunt, 2006
Soybean	11.07	5	Malek et al., 2012; DPIF, 2008
Silvergrass	12.67	2	Iqbal et al., 2015; Jorgensen, 1996
Poplar	9.54	7	Aylott et al., 2008; Walle et al., 2007
Willow	9.51	8	Aylott et al., 2008; Walle et al., 2007
Switch grass	11.69	4	Hattori & Morita, 2010; Wullschleger, et al., 2010.
Cattails	12.65	3	Dubbe et al., 1988; Suda et al., 2009.

4.3.1.5 Rooting system

Data for this category were mainly an adaptation from Canadell et al. (1996) as explained in section 3.2.4.5. However, for the other three species (Indian mustard, silvergrass and cattails) not covered in the global comprehensive study, the protocol described in Figure 3.3 was followed. As shown in Table 4.5, sunflower and switchgrass had the best maximum root depth, followed closely by willow, silvergrass and poplar. A major drawback of phytoextraction is that implementation is usually on sites where contamination is shallow. This is further exacerbated by the fact that over 47% of the agricultural land in Europe has a problem of low rooting depth of plants (Gerwin et al., 2018). Deeper roots mean deeper levels of contamination can be accessed to improve treatment efficiency. In addition to their usefulness for phytoremediation, plants root depth has significant implications for carbon and nutrient cycling, ecosystem hydrological balance and plant's ability to tolerate harsh environmental conditions like drought (Paz et al., 2015). This can also enhance phytoremediation indirectly. Generally, roots of trees grow deeper to create hydraulic control and clean up deeper lying soil contaminations (EPA, 2022). For this study however, it was shown that mammoth sunflower can have very deep taproot systems with hairy secondary roots that can go about 2.7 m below the ground (Weaver, 1926). This can aid phytoextraction to a large extent. While forest trees generally have deeper, more developed roots, their slow growth rate makes them undesirable for phytoremediation, unless for large scale long-term projects.

Table 4. 5 Mean root depth of the different species

Species	Maximum rooting depth (m)	
	Depth	Rank
Sunflower	2.7	1
Indian mustard	1.2	7
Soybean	1.8	6
Silvergrass	2	4
Poplar	1.9	5
Willow	2.2	3
Switch grass	2.7	1
Cattails	1	8

4.3.1.6 Second generation attribute (SGA)

As earlier stated, data were obtained from the PFAF database; a compilation of plant information spanning over 7000 plant species with information on plant uses and their most important features. Based on the PFAF database, edibility ratings are assigned to plants. Edibility ratings shown in table 4.6 are an adaptation from PFAF (2019) where they ranked plant species from 1 – 5 (minor to great) based on their desirability as food for humans. The lower the edibility ratings, the higher their second-generation attribute. The edibility ratings of the different species were compared, and their second-generation appeal were compared and ranked in Table 4.6. Poplar, willow and silvergrass had the best SGA. However, most of the species under review are not considered primary food sources for most people.

Table 4. 6 Plant species food uses and edibility rating. (source: PFAF, 2017)

Species	Food uses				Edibility rating	Rank
	Seeds/Fruits	Leaves/Flowers	Roots/Tubers	Stems		
Sunflower	Edible	Edible	Not	Edible	5	8
Indian mustard	Edible	Edible	Not	Edible	4	5
Soybean	Edible	Edible	Not	Not	4	5
Silvergrass	Not	Not	Not	Edible	1	1
Poplar	Not	Not	Not	Edible	1	1
Willow	Not	Not	Not	Edible	1	1
Switch grass	Not	Not	Not	Not	2	4
Cattails	Edible	Edible	Edible	Edible	4	5

4.3.1.7 Crop growth rate (CGR)

Species' CGR data from the searches were collated, analysed and their means were computed. These CGR data were compared according to performance and ranked. The higher the mean CGR value, the higher the performance rating. While biomass yield is important for every phytoremediation/bioenergy project, how quickly a species attain the desired yield level is equally important. Growth rate describes an increase in biomass over a unit of time. As highlighted in Table 4.7, silvergrass, sunflower and switchgrass had the best growth rates while poplar and willow being woody crops has the least growth rate among species under comparison. Herbaceous plants typically grow faster than woody plants and when contaminated with heavy metals, some perennial grasses like silvergrass and switchgrass can still sprout even after shoot harvest (Gilabel et al., 2014).

Table 4. 7 Mean plant species crop growth rate

Species	CGR ($gm^{-2}d^{-1}$)	Rank	Selected references (See Appendix for full reference list)
Sunflower	9.11	2	Panneerselvam & Arthanari, 2011; Tribouillois et al., 2015
Indian mustard	4.76	6	Panda et al., 2004; Tribouillois et al., 2015
Soybean	8.52	4	Buttery, 1969; Addo-Quaye et al., 2011; Rahman et al, 2011
Silvergrass	24	1	o Di Nasso et al., 2011; El Bassam, 2010
Poplar	0.11	8	Lamers et al., 2006
Willow	0.06	7	Lamers et al., 2006
Switch grass	8.77	3	El Bassam, 2010; o Di Nasso et al., 2011.
Cattails	6.83	5	Kvet (1971); Dykyjova (1971)

4.3.1.8 Yield index (YI)

Sourced data for drought tolerance were aggregated, their means computed, and comparisons were made. Data on species water stress tolerance and their associated ranking are in the appendix section. As seen in Table 4.8, sunflower, Indian mustard and soybean had the best drought tolerance. Drought tolerance however is relative to the level of drought the plants are exposed to. When continually exposed to higher levels of drought, at some point, the plants will die. Drought tolerance is becoming a critical criterion due to the associated environmental impacts of climate change and the cost implications of adopting high-powered irrigation systems especially in poorer communities (Rauf, 2016). Apart from cattails, most of the species compared have decent resistance to water stress at maturity. The effect on productivity is minimal.

Table 4. 8 Mean Yield index of the various plant species

Species	Mean DTI	Rank	Selected references (See Appendix)
Sunflower	62.65	2	Ahmad et al., 2009; Saensee et al., 2012
Indian mustard	65.63	1	Moghaddam & Pourdad et al., 2010; Moradshahi et al., 2004
Soybean	62.53	3	Ohashi et al., 1999; Sunaryo et al., 2016
Silvergrass	58	4	Mann et al., 2013
Poplar	54.75	5	Larchevêque et al., 2011; Tschaplinski et al., 1994
Willow	48.80	6	Nakai et al., 2010
Switch grass	43.67	7	Barney et al., 2009
Cattails	19.77	8	Asamoah & Bork, 2010; Dubbe et al., 1988

4.3.1.9 Metal Tolerance Index (MTI)

Few studies have been carried out on metal tolerance for the various plants and metals under investigation so the data available were collected, collated, averaged, the min-max values were derived, and comparisons were made. The mean data and ranks of the different species were summarized in section 4.9. Switchgrass had the best metal tolerance, followed by woody crops poplar and willow. Woody plants when established tends to tolerate heavy metal contamination more and they are particularly more advantageous over herbaceous plants in this regard as they are not restricted by multi-element polluted sites (Rabêlo et al., 2021)

Table 4. 9 Average metal tolerance index of the various plant species

Species	Average MTI	Rank	Selected references (See Appendix)
Sunflower	430	6	Shi & Cai, 2009; Rivelli et al., 2012
Indian mustard	98.22	7	Lee, 2003; Singh et al., 2017
Soybean	94.36	8	Malan & Farrant et al., 1998
Silvergrass	255.72	4	Guo et al., 2016; Arduini et al., 2006;
Poplar	354.70	3	Zacchinni et al., 2011; Utmazian et al., 2007
Willow	412.06	2	Zacchinni et al., 2011; Hakmaoui et al., 2006
Switch grass	114.54	1	Chen et al., 2012; Zhang et al., 2015
Cattails	199.68	5	Ye et al., 1997

4.3.2 Multi-criteria analysis matrix

Based on the selected phytoremediation species, a decision matrix was developed according to the selected suitability criteria and their corresponding performance index earlier highlighted. Based on the various assigned weight of the criteria, aggregate weighted scores were generated, from which judgement can be made on species overall performance. Exploratory analysis of table showed no problems of data dependency (i.e., robustness) (Pavlicic, 2000). Rankings are regarded as robust when the addition or removal of an alternative(s) does not alter the classifications of the other alternatives (Cinelli et al., 2014). Sunflower and silvergrass emerged as top candidates in that order for a combined use as both phytoremediation crops and bioenergy source as shown in Table 4.10. Indian mustard and cattails were the two worst performers based on the studies aggregated. While the Indian mustard is a good phytoextraction species, they are deficient as energy crops. Their lignocellulosic content, poor rooting depth makes them relatively undesirable for a combined phytoextraction/bioenergy use. Cattails are good for biomass production, have poor drought tolerance and are average at most other criteria. Also, the total scores are also influenced by the weights of the criteria and not solely on performance (see Table 4.10 and 4.11). Table 4.11 shows species performances when priorities are not given to specific criteria. Overall rankings of species performance changed with application of priority weightings. This also gives an indication of the sensitivity of the matrix to weightings. However, full scale sensitivity analysis was not carried out in this study.

Table 4. 10. Multicriteria decision matrix when normalized and weighted

Criteria	Key indicator	Plant species								Weighting score
		Sunflower	Indian mustard	Soybean	Silver grass	Poplar	Willow	Switch grass	Cattails	
Pollutant accumulation	Translocation factor	0.0921	0.1009	0.1500	0.0624	0.1013	0.0474	0.0138	0.0000	0.15
Growth rate (Short rotation)	Crop growth rate (CGR)	0.1134	0.0589	0.1060	0.3000	0.0006	0.0000	0.1091	0.0848	0.30
Root system	Root depth	0.0500	0.0059	0.0235	0.0294	0.0265	0.0353	0.0500	0.0000	0.05
Metal tolerance	Metal tolerance index	0.0060	0.0012	0.0000	0.0481	0.0776	0.0947	0.1000	0.0314	0.10
Biochemical composition	Lignocellulosic biomass	0.0414	0.0000	0.0139	0.0332	0.0455	0.0500	0.0195	0.0215	0.05
Biomass production (tons per acre)	Total dry biomass (matter) yield	0.2500	0.0051	0.0566	0.1147	0.0011	0.0000	0.0791	0.1139	0.25
Thermal energy potential	Calorific value in MJ per kg	0.0243	0.0241	0.0000	0.0248	0.0500	0.0393	0.0023	0.0207	0.05
Drought tolerance	Yield Index	0.0467	0.0500	0.0466	0.0417	0.0381	0.0316	0.0260	0.0000	0.05
Total scores		**0.6239**	**0.2460**	**0.3967**	**0.6541**	**0.3407**	**0.2983**	**0.3999**	**0.2724**	1
Rankings		**2**	**8**	**4**	**1**	**5**	**6**	**3**	**7**	

The cells in the matrix contains species min-max normalized and already weighted values and gives an indication of species performance in relation to each individually defined criterion. Min-max is measured as
Min-max = (x-min)/(max-min) where min and max are the minimum and maximum values given its range
Aggregate weighted score = $W_1X_1 + W_2X_2 ... W_nX_n$. where W = relative weight and X = min-max

Table 4. 11. Multicriteria decision matrix when normalized but not weighted

Criteria	Key indicator	Plant species								Weighting score
		Sunflower	Indian mustard	Soybean	Silver grass	Poplar	Willow	Switch grass	Cattails	
Pollutant accumulation	Translocation factor	0.6137	0.6725	1.0000	0.4160	0.6754	0.3163	0.0918	0.0000	0.15
Growth rate (Short rotation)	Crop growth rate (CGR)	0.3780	0.1963	0.3534	1.0000	0.0021	0.0000	0.3638	0.2828	0.30
Root system	Root depth	1.0000	0.1176	0.4706	0.5882	0.5294	0.7059	1.0000	0.0000	0.05
Metal tolerance	Metal tolerance index	0.0601	0.0115	0.0000	0.4808	0.7757	0.9465	1.0000	0.3138	0.10
Biochemical composition	Lignocellulosic biomass	0.8282	0.0000	0.2787	0.6636	0.9107	1.0000	0.3898	0.4299	0.05
Biomass production (tons per acre)	Total dry biomass (matter) yield	1.0000	0.0203	0.2264	0.4586	0.0044	0.0000	0.3164	0.4557	0.25
Thermal energy potential	Calorific value in MJ per kg	0.4860	0.4829	0.0000	0.4953	1.0000	0.7850	0.0467	0.4143	0.05
Drought tolerance	Yield Index	0.9346	0.9996	0.9320	0.8333	0.7624	0.6327	0.5209	0.0000	0.05
Scores (norm..)		**5.3006**	**2.5007**	**3.2611**	**4.9358**	**4.6601**	**4.3865**	**3.7295**	**1.8965**	1
Rankings		**1**	**7**	**6**	**2**	**3**	**4**	**5**	**8**	

4.3.3 Result synthesis

Findings from the preliminary selection procedure carried out in section 3.2.2 suggests that all eight species evaluated in the study have in the least some bioremediation and phytoremediation properties. The study however was to establish which ones best combine both characteristics. The major energy generation properties identified are calorific value, biochemical composition, and biomass production. On the other hand, metal tolerance and translocation index are the primary important properties of a good phytoremediation crop. However, other important properties of an ideal phytoremediation crop like growth rate, drought tolerance and root system were factored in.

Sunflower shows very good calorific value, the ideal biochemical composition ratio and great biomass productivity. It also shows it has some beneficial phytoremediation properties with good translocation index and some strong performance in relation to metal tolerance. Silvergrass also shows similar performances in these combined properties. A popular and important phytoremediation crop like Indian mustard showed good phytoremediation capabilities but falls short in important bioenergy properties (lignocellulosic content, biomass yield) in relation to the other plants. Even though this research was tailored towards comparing species against multiple properties, its findings can aid decision making for specific plant property needs.

4.3.4 Application

The gathering of quantitative data from multiple research projects globally is usually contentious because results are influenced by multiple, sometimes unforeseen factors. For example, comparing growth rates of same species grown at different environmental conditions may be misleading as these conditions play a significant role on how these species grow. For most studies, precautions to address this problem are put in place, exclusion criteria are set, adjusted equations are developed but it is difficult to state with utmost certainty that this problem is eliminated. However, very meaningful inferences can be drawn from these findings when the limitations are recognized and steps to minimize these limitations are put in place.

A multicriteria decision matrix in its simplest form summarizes findings based on information gathered after an evaluation of a plethora of conflicting criteria. In some cases, these information on given criteria are merely opinions and not backed by quantitative data. In these cases, utility scores are assigned to criteria which are sometimes derived by collaborative stakeholder consultations and analysis or sometimes questionnaire inputs or even computer modelling. However, for this study, quantitative data were derived from multiple independent research globally. It is also important to note that criteria for the most part, are seldomly considered equally. Some are considered more important than others in decision making, hence the need to assign weights. The weights assigned to criteria greatly determines to a large extent the outcome of the analysis (See Table 4.10 and Table 4.11).

In scenarios involving quantitative data comparison, it is recommended that an independent study be carried out where possible, exposing all options to the same conditions to make a fairer comparison with limited external influence. This however is often impossible in cases of multiple options, hence the need for a multicriteria analysis for an informed evidence-based decision-making.

The chapter aimed to explore the feasibility of MCDA as a tool for deciding the best plant species for synergy between two primary uses: phytoremediation and bioenergy generation. Results showed varying degrees of species' strengths in relation to the specified criteria and their weaknesses where present. However, the broader study aims to go beyond just evaluating MCDA as a tool for exploring decision making options to making decision based on the findings and seeking to validate the outcomes of the MCDA process.

The top candidates from the MCDA process were sunflower and silvergrass but only sunflower will be further explored via a phytoremediation study in chapter five to seek to validate its metal accumulation properties and a pyrolysis process to assess its bioenergy generation and biochar potential. This was due to the challenges of germinating silvergrass as germination takes approximately 10 – 90 days (given the short planting window in the spring).

4.3.5 Conclusion

A systematic MCDA process which involved developing a matrix to summarize numeric data sourced from scientific databases was used to select plant that best combine phytoremediation and bioenergy generation properties. For this study, sunflower and willow emerged as the best candidates for optimal phytoremediation and energy generation.

A look at the multicriteria matrix scores assists the process of making decisions because they compile plant species options quantitatively for all relevant criteria and KPIs. An MCDA should only be used when selection options are many and the feasibility of carrying out independent studies is low. The use of more advanced MCDA methods is widespread among experts, but its usage is sometimes associated with lack of transparency in terms of their decision rules (i.e., their workings are difficult to grasp by non-specialists) (Kaliszewski & Podkopaev, 2016). The Weighted Sum Model as utilized in this study to offer a simplistic, easy to grasp level ground to interpret and make inferences on results and rankings of decision alternatives. By this, decision makers can interpret results in much simpler terms than offered by more advanced MCDA methodology. By bounding data within a common scale, the model also dealt well with outliers. The model can be further optimized by the application of a variety of different weighting to fully analyse its sensitivity. The weighting process helps incorporate stakeholder priorities to the selection process. Also, the suitability criteria employed in study is not designed to be exhaustive. Additional suitability criteria can be considered according to the user's specified objectives (for e.g., tolerance to flooding, soil pH, water balance etc.). The model is also designed to be adaptive to other forms of phytomanagement like phytostabilization, rhizofiltration or regeneration of brownfield sites.

CHAPTER FIVE

5.0 PHYTOEXTRACTION OF METAL-CONTAMINATED SOIL USING *HELIANTHUS ANNUUS* (SUNFLOWER)

5.1 Background

With the large and increasing size and scope of metal related environmental problems, the phytoextraction of metals from soils and water presents a huge economic opportunity for green sustainable remediation. As mentioned in Section 1.1 of this thesis, considering human population increase, scarcity of agricultural land, increased rate of mining and industrialization and consequently a significant jump in the rates of metal accumulation in the earth crust, an efficient and sustainable means of remediating contaminated land is in pressing need. Metal pollutants are different from most organic contaminants as they do not biodegrade and so pose serious threat to living things and the environment alike, as some of them are carcinogenic and mutagenic compounds with destructive properties (Wu et al., 2018). At very high concentrations, metals can have very negative effect on plants growth and productivity.

Plants tolerance to metal contaminants differ markedly; most plants react poorly to the presence of metals in their tissues as these contaminants cause disruptions to plant cellular activities (Peixoto et al., 2001). Because of this, desired plants for phytoextraction are usually hyperaccumulators. Hyperaccumulator plants are known for their ability to concentrate high volumes of essential and nonessential contaminants on to their tissues (Baker and Brooks, 1989). Because these metals cannot be degraded, the clean-up process usually requires removal or extraction. Therefore, plants with capabilities to extract metals from soils are what is desired. In addition to hyperaccumulating properties, the desired plant should also meet other important criteria like fast growth rate, high biomass production and metal tolerance as earlier described in section 1.1 of chapter 2.

Helianthus annuus (sunflower) is an annual plant indigenous to Native America, belonging to the Asteracea family. The stem of the plant can grow up to 3m with flowering head diameter possibly reaching up to 30cm in diameter (Alaboudi et al., 2018). From the multicriteria analysis study carried out in Chapter 4, *H. annuus* has been shown to possess good phytoremediation properties like fast growth rate, resistance to metal contaminants, good metal accumulation potential and good biomass production. In addition, they have also been shown to have good bioenergy features like high calorific value and good lignocellulosic properties. This study is therefore aimed at assessing the metal-remediation properties of *H. annuus* using some widely studied heavy metals. In addition, it aims to aid metal uptake by maximizing the growth performance of *H. annuus* using some biological growth promoting mechanism.

A veritable means by which the growth performance and metal accumulation of plants can be enhanced is via its combination with growth promoting microorganisms, specifically bacteria. Plant growth promoting bacteria (PGPB) or plant growth promoting rhizobacteria (PGPR) as they are sometimes called, are beneficial plant bacteria that generally influence plant growth positively. They can affect plant growth directly by aiding the synthesis of phytohormones and increasing nutrient availability for plants or they can affect plants indirectly by suppressing the effect of phytopathogens (Kong & Glick, 2017). Most of these plant-microorganism interactions happen in the rhizosphere. Common rhizobacteria such as *Pseudomonas* and *Bacillus spp.* are usually found in the rhizosphere of a host of plants. *Pseudomonas spp* are the most widely researched rhizobacteria as plant growth promoters (Godino et al., 2016). When compared to Pseudomonas, *Bacillus spp.* are significantly less studied but have still been widely explored in the literature for their plant growth promoting properties (Sansinenea, 2019) as well as their ability as metal accumulation enhancers (Jan et al., 2022)

Bacillus aryabhattai is a soil bacterium first isolated and identified in 2009 from cryotubes used to collect air samples (Shivaji et al., 2009). Some of its strains has since been isolated from soils of rice, sugarcane, and dense forest soils (Pailan et al., 2015; Tanamool et al., 2013; Chanasit et al., 2014). They have also been isolated from an urban tunnel (Park et al., 2012), and from deep sea water (Wen et al., 2015). Its plant growth promoting ability have been demonstrated in studies using model plants like *Xanthium italicum* (Lee et al., 2012) and *Zea mays* (Bhattacharyya et al., 2017). Plant biomass production (especially under biotic or abiotic stress) is an indirect means of measuring plants metal tolerance and ultimately gives an indication of plants metal accumulating potential. Given its growth promoting potential, *B.*

aryabhattai's capacity to enhance metal accumulation via its association with plants have not been previously tested. This study will seek to promote productivity and consequently, metal uptake of *H. annuus* using *B aryabhattai* strain, AB211.

5.2 Aim and Objectives

The aim of this chapter is to examine the phytoremediation potential of *H. annuus* for the remediation of soils contaminated with Cd, Pb and Zn. Some objectives set to achieve this aim are:

- To observe the growth response of *H. annuus* in soils contaminated with Cd, Pb and Zn in relation to metal-free ones.
- To quantify the above ground tissue metal concentration of *H. annuus* in soils contaminated with Cd, Pb and Zn and consequently determining their metal uptake and tolerance levels.
- To investigate the response of *H. annuus* to the addition of *Bacillus aryabhattai* strain (AB211) to both metal-contaminated and uncontaminated soils.

5.3 Result and discussions

5.3.1 Soil properties

The soil utilised for the study is Kettering soil classified as loam soil with pH ranging from neutral to slightly basic, determined with the aid of a standard 'feel' test (Thien, 1979). The mean values of the different soil properties tested are enumerated in Table 5.1. The physico-chemical properties of this soil are well established in literature (typically Soil organic matter (SOM), 3-7%, pH, 6.8-7.3) (Lowe et al., 2016; Moragues-Saitua et al., 2019). The measured SOM and pH match expected values in literature, 3.9±0.2 and 6.8±0.03 respectively. The influence of soil pH on nutrient availability and uptake is very profound, with most soils used for crop production having soil pH ranging from slightly acidic to slightly basic (pH 6-8) (Läuchli & Grattan, 2017). Even though SOM makes up a small percentage of most soils, its effect on soil productivity is very significant as it influences soil water holding capacity, stability, structure, and nutrient storage (Bauer & Black, 1994). Agricultural lands typically have SOM ranging from 1-6% (Bauer & Black 1994). The measured physical properties of Kettering soil as shown in Table 5.1 are at a level very ideal for plant and microbial growth. It has been reported that during a combined plant-microbial phytoremediation process, the presence of microbes can alter plants physiological processes thereby impacting their adaptation to stress (Ren et al., 2019). These strains at the right numbers can potentially change the rhizosphere structure of soils in ways that enhance biomass production of plants and thereby improving plant remediation performance (Ashraf et al., 2017). It is essential that soils used for phytoremediation purposes have the ideal population of soil microorganisms to attain optimum results. The initial microbial counts of dry soil shown in Table 5.1 are considered to fall within the ideal range (He & Yang, 2007).

Table 5. 1. Soil properties of Kettering soil used for phytoremediation experiment

Soil sample	**Kettering**
pH	6.8 ± 0.03
Temperature (^{0}C)	22.5 ±0.04
Soil organic matter (%)	3.9 ± 0.2
Soil moisture content (%)	15.63 ± 0.2
Pb (mg/kg)	0.020±0.002
Zn (mg/kg)	0.029±0.002
Bacteria (cfu g^{-1})	3.9 x 10^4
Fungi (cfu g^{-1})	5.2 x 10^3
Actinomycetes (cfu g^{-1})	5.8 x 10^4
CEC	11.67 ± 0.03
Dry bulk density	1.34

5.3.2 Effects of heavy metal stress on *H. annuus* growth

When plants are exposed to high concentrations of heavy metal contamination, there is an increased likelihood for damage to several metabolic activities necessary for plant health, leading to potential death of plants. Plants exposure to excess levels of heavy metals can lead to inactivation of photosystems (Paunov et al., 2018), inhibition of physiologically active enzymes (Gadd, 2007), and the destruction of mineral metabolism (Janas et al., 2010). As mentioned earlier in Section 3.3.4.4 of this thesis, biomass production is a crucial criterion for any good phytoremediation species as it is directly linked to its ability to take up toxic metal contaminants at high rates. From the MCDA study carried out in Chapter 4 of this thesis, *H. annuus* emerged as a top performer. The MCDA results suggests *H. annuus* have good biomass productivity, fast growth rate and a capacity to remove metals from contaminated soils.

The growth of sunflower under different levels of heavy metal contamination was observed. Dry biomass and metal tolerance index (Figure 5.1 & Table 5.2) highlighted the effects of a set of heavy metals on the growth of sunflower plants. Experiment was run for 10 weeks as this represents the typical duration to achieve sunflower bloom and maturity (Andersen, 1975). Plants in experiment were fully matured with emerged flowers by week 10.

Plants appears to show healthy growth patterns in the control as well as for the treatment inoculated with only *B. aryabhattai* AB211. Plants amended with Zn also showed relatively more metal tolerance than the rest of the plants with metal treatments, followed closely by Pb tolerance. However, for plants grown in Cd and Cd+Pb+Zn soils, the effects are very pronounced. There is visible stunted growth and discoloration. These plants have significantly less root and shoot biomass as well as very low metal tolerance index. This marked difference is consistent for both the regular sunflower plants and the ones inoculated with *B. aryabhattai* AB211. Even though the plants with *B. aryabhattai* AB211 performed slightly better, the growth patterns observed across different levels of metal treatments are similar and consistent.

The prevalence of heavy metals stress affected the growth and metabolism of sunflower plants at varying degrees. Concentrations of Cd and Cd+Pb+Zn above the documented threshold (EPA, 2007) led to visible stunted growth, depleted biomass production and some discoloration. This is consistent with findings reported in other phytoremediation works with sunflower and other plant species (Alaboudi et al., 2018; Gajewska & Sklodowska, 2007; Tewari et al., 2002). The presence of Cd in soils have also been reported to have negative effect on growth of soybean and chickpea (Dowdy & Ham, 1977; Hasan et al., 2007). The combined effect of Cd, Pb and Zn are similar in indicative effects to Cd. Plants were adversely affected by the presence of multiple metals as shown. With a tolerance index of 10.87 %, the effects were no different from when Cd is in effect in isolation. Sunflower had the best tolerance when treated with Zn than in any of the metals under study as shown in the data in Table 5.2, with its tolerance index at 74.35%. With a metal tolerance index of 45.65 % and 45.44 % (for treatment with *B. aryabhattai* AB211), plants amended with Pb showed average tolerance. Early patterns of growth showed minimal Pb effects, but the effect became more pronounced as plants grew older. Plants amended with Pb have been reported to have cumulative, slow, and subtle effects at the early stages of contamination (Sharma and Dubey, 2005). The substantive elements of these results are consistent with some of the findings in the multicriteria analysis matrix earlier developed in chapter 4.

5.3.3 Effects of AB211 strain on plant growth under different metal treatments

The effects of metal contamination were investigated for different metal treatments in the presence and absence of a bacterial strain, *B. aryabhattai* AB211. Evidence from Figure 5.1 and Table 5.2 suggests plants with the bacterial strain *B. aryabhattai* AB211 appears to be more resilient to metal stress than ones without especially for Cd and the combination of Cd, Pb and Zn. Root development appears more profound in plants with the strain than those without. From dry weight evidence in Table 5.2, sunflower again shows very pronounced resilience to Pb and Zn contamination even at documented phytotoxic levels (EPA, 2007) both in the presence and absence of the bacterial strain. However, growth performance was significantly better for Pb, and Zn sunflower species inoculated with *B. aryabhattai* AB211 strain than for those without, H_0 (p<0.05). Again, the effect of Cd and a combined effect of Cd, Pb and Zn are similar. Also, there was no significant difference in dry weight in the combined treatment (Cd+Pb+Zn) with strain and without strain even though treatment with strain was slightly higher in biomass production than without, after 10 weeks, H_0 (p>0.05). The combined effects of all treatments with *B. aryabhattai* AB211 and those without shows a significant difference in total dry biomass production after 10 weeks (p<0.05). However, when shoot production is separated from root production, there is no significance in root production for plants with *B. aryabhattai* AB211 and those without (p>0.05).

On evidence, the bacterial strain *B. aryabhattai* AB211 has significant effect in promoting plants growth and help plants build comparative resilience to metal contamination. Plant growth promoting bacteria (PGPB), *B. aryabhattai* AB211 may have directly promoted growth by aiding and facilitating the acquisition of resources in soils or via plant hormones level modulation but can also be indirectly via reducing the inhibitory effects of some soil pathogens that could have stifled plant growth (Glick, 1995; Glick, 2012). Bhattacharyya et al. (2017) carried out a genome sequencing and annotation study as well an experimental demonstration and reported that *B. aryabhattai* AB211 is metabolically diverse and possess properties that is tremendously beneficial to plant growth. As reported in section 5.1 of this thesis, it has also been shown to promote growth in plants like *Xanthium italicum* (Lee et al., 2012) and Zea Mays (Bhattacharyya et al., 2017). The mechanism of plant growth promotion is discussed in more detail in Section 5.3.4.

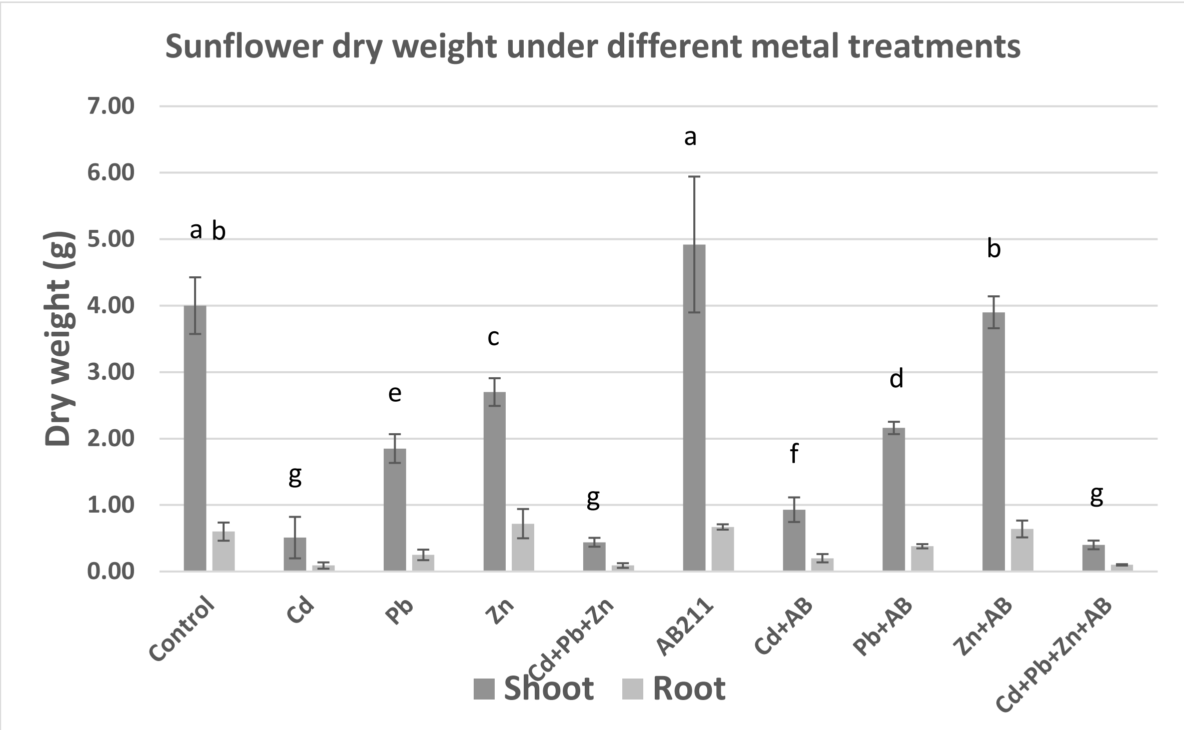


Figure 5. 1. Dry weights of sunflower plants grown in soils with different variations of Cd (50 mg/kg), Pb (300 mg/kg) and Zn (600 mg/kg) contamination after 10 weeks. Data are given as means of three replicates ± Standard deviation (SD). Cd: cadmium, Pb: lead, Zn: zinc, AB: *B. aryabhattai* AB211. Treatment bars that do not share a letter are significantly different

Table 5. 2. Biomass production of *H. annuus* under different metal treatments and their associated metal tolerance index

Treatments	Dry matter yield (g)		Metal tolerance index (%)
	Shoot (Mean $\pm$ SD)	Root (Mean $\pm$ SD)	
Control	4.00 $\pm$ 0.43	0.60 $\pm$ 0.14	_____
Cd	0.51 $\pm$ 0.31	0.09 $\pm$ 0.05	13.04
Pb	1.85 $\pm$ 0.22	0.25 $\pm$ 0.08	45.65
Zn	2.70 $\pm$ 0.21	0.72 $\pm$ 0.22	74.35
Cd+Pb+Zn	0.44 $\pm$ 0.07	0.09 $\pm$ 0.04	11.52
AB211	4.92 $\pm$ 1.02	0.67 $\pm$ 0.04	_____
Cd+AB	0.93 $\pm$ 0.19	0.20 $\pm$ 0.06	24.57
Pb+AB	2.16 $\pm$ 0.09	0.38 $\pm$ 0.03	55.22
Zn+AB	3.90 $\pm$ 0.24	0.64 $\pm$ 0.13	98.70
Cd+Pb+Zn+AB	0.40 $\pm$ 0.07	0.10 $\pm$ 0.01	10.87

Data are given as means of three replicates $\pm$ Standard deviation (SD). Cd: cadmium, Pb: lead, Zn: zinc, AB: *B. aryabhattai* AB211.

5.3.4 Heavy metal accumulation of *H. annuus* under different metal treatments and the role of PGPB, *B. aryabhattai* AB211

The metal accumulating potential of *H. annuus* and the effect of *B. aryabhattai,* AB211 on its phytoextraction capabilities were tested using pot trials in a greenhouse. Species bioconcentration factor and translocation factor are generally good indicators of their hyperaccumulating potential (Eribo et al., 2022). To be termed a hyperaccumulator plant, a plant species typically requires its translocation factor and bioconcentration factor above 1 (Ghori et al., 2016). In this study, bioconcentration and translocation factors for *H. annuus* not inoculated with *B. aryabhattai* AB211 ranges from 0.81 – 0.94 indicating the suitability of *H. annuus* as an accumulator for heavy metal, even though it just falls short of the required hyperaccumulator status. However, when inoculated with *B. aryabhattai* AB211, bioconcentration and translocation factors ranged from 1.0 – 1.31, which represents a 19 – 37% improvement to its metal accumulation, therefore attaining hyperaccumulator status. The disparity in accumulation between ones with the *B. aryabhattai* AB211 and those without was much more in Cd contaminated plants than in others ($p<0.05$). On the capacity to accumulate heavy metal, *H. annuus* performance was in the order, Cd > Pb > Zn. This hierarchy of accumulation rates is also supported by Niu et al. (2007) who reported the rate of accumulation of Cd (20 mg/L) to be higher than Pb (100 mg/L) also using *H. annuus* as its model phytoremediation species. On dry weight evidence, Cd was also among the most affected with metal accumulation, may be in part due to the faster rate of accumulation on to its plant tissues.

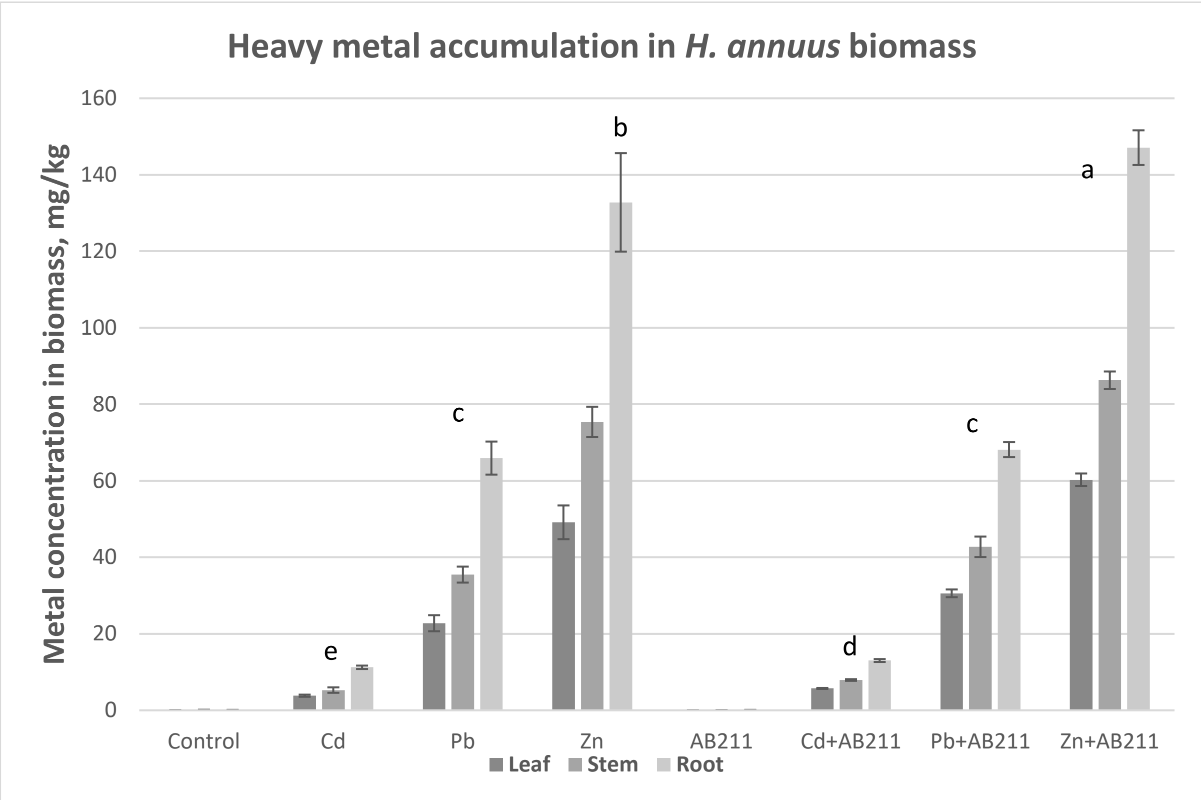


Figure 5. 2 Metal accumulation of sunflower plants grown in soils with Cd (50 mg/kg), Pb (300 mg/kg) and Zn (600 mg/kg) contamination after 10 weeks. Data are given as means of three replicates ± Standard deviation (SD). Cd: cadmium, Pb: lead, Zn: zinc, AB211: *B. aryabhattai* AB211. Treatment bars that do not share a letter are significantly different

Table 5. 3. *H. annuus* bioconcentration and translocation factors

Treatments	Bioconcentration factor (Mean ±SD)	Translocation factor (±SD)
Control	----	----
Cd	0.83 ± 0.03 d	0.81 ± 0.03 d
Pb	0.88 ± 0.01 c	0.89 ± 0.10 c
Zn	0.85 ± 0.07 c, d	0.94 ± 0.04 c
AB211	----	----
Cd+AB211	1.31 ± 0.06 a	1.05 ± 0.03 a
Pb+AB211	1.16 ± 0.04 b	1.08 ± 0.04 a
Zn+AB211	1.15 ± 0.03 b	1.00 ± 0.02 b

Data are given as means of three replicates ± Standard deviation (SD). Cd: cadmium, Pb: lead, Zn: zinc, AB211: *B. aryabhattai* AB211. Treatments that do not share a letter are significantly different (P<0.05).

Note: Bioconcentration factor = $\frac{Metal\ concentration\ in\ plants}{Metal\ concentration\ in\ soil}\ x\ 100$……………….Equation 5.1

Translocation factor = $\frac{Metal\ concentration\ in\ shoot}{Metal\ concentration\ in\ root} x\ 100.$ ……………………………..Equation 5.2

Metal uptake by plant was measured using the mass balance method (i.e., weighting metal uptake in plant shoots/roots according to their respective masses). See Table 5.4 and 5.5 for metal content data of sunflower with and without AB211.

Table 5. 4 Metal concentration of sunflower plants and soil post remediation (no AB211)

	Cd (mg/kg) (Mean ± SD)	Pb (mg/kg) (Mean ± SD)	Zn (mg/kg) (Mean ± SD)
Shoot	9.11 ± 0.49	58.24 ± 2.10	124.54 ± 4.19
Root	11.25 ± 0.44	65.94 ± 4.32	132.79 ± 4.25
Soil	24.58 ± 1.22	142.17 ± 3.96	305.10 ± 12.86

Table 5.5 Metal concentration of sunflower plants and soil post remediation (with AB211)

	Cd (mg/kg) (Mean $\pm$ SD)	Pb (mg/kg) (Mean $\pm$ SD)	Zn (mg/kg) (Mean $\pm$ SD)
Shoot	13.64 $\pm$ 0.18	73.33 $\pm$ 1.84	146.55 $\pm$ 1.97
Root	13.03 $\pm$ 0.38	68.12 $\pm$ 1.97	147.09 $\pm$ 4.54
Soil	20.37 $\pm$ 0.75	121.71 $\pm$ 2.70	255.42 $\pm$ 6.08

Over this experiment, the performance of *H. annuus* with respect to metal tolerance and accumulation differs for the different metals. For example, the enrichment level of Cd by the plant could be influenced by a few physiological factors, such as uptake rate from soils, the rate of xylem translocation from root to aboveground part of plants, and cadmium sequestration in organic complexes or subcellar compartments (Hart et al., 1998). Bioaccumulation and translocation patterns are not solely dependent on species alone, but also on the metal types and environmental factors.

The experiment also showed that heavy metal effects on plants are markedly dissimilar. The effect was much more pronounced in Cd than in any other metals. Even though the phytotoxicity of Cd is well established, the mechanism of effect is still to be fully understood (Pandey et al., 2009). The effects of Cd on the plants could be as a direct result of the deleterious effects of cadmium to the biochemical mechanism that ensures cell survival (Niu et al., 2007). Plants are affected by Cd due to its effect in inhibiting respiration and photosynthesis, reduction in nutrient and water uptake, alterations in protein and gene expressions, inhibition of beneficial enzymes, metabolism disturbance, enhancement of lipid peroxidization and enhancement of reactive oxygen species accumulation (Tanhan et al., 2007; Shanmugaraj et al., 2019). The tissue damage expression was visible in plants with cadmium in the form of leaf colouration and stunted growth. Regardless of damage, *H. annuus* was still effectively accumulating Cd at level higher than reported by Clemente et al. (2021).

When in a combined synergistic association with plants, PGPB can regulate routine physiological processes of plants to limit stress imposed on plants by heavy metals while simultaneously dissolving insoluble heavy metals via several metabolic processes as highlighted by Sessitsch et al. (2013). Indirectly, PGPB can also regulate the bacterial community structure of the rhizosphere soil to improve biomass production and consequently, phytoremediation. The *B. aryabhattai* strain AB211 was only first isolated in 2009 (Shivaji et al., 2009) and the first attempt at understanding its plant growth promoting potential was carried out by Lee et al. (2012) using *Xanthium italicum* and subsequently by Bhattacharyya et al. (2017) using *Zea mays* as model plant. On both cases, the argument for its benefit as a plant growth promoter is overwhelming. The role of the *B. aryabhattai* AB211 in improving metal accumulation by *H. annuus* was investigated and there was a significant difference in uptake levels for Cd, Pb and Zn when *B. aryabhattai* AB211 was applied than when it was not ($p<0.05$). In general, the results showed that inoculating the plants with *B. aryabhattai* AB211 promoted *H. annuus* growth, improved the dry weight of the aboveground biomass, and increased metal accumulation.

The success of a phytoextraction process depends mostly on the plant and the bioavailability of the target metal but could also be influenced by the interaction between the plants and its surrounding microorganisms (Chen et al., 2013). It has been reported that bacteria can help enhance metal bioavailability in soil (Sheng et al., 2012). The root of plants, and the bacteria in soil, and their synergistic interactions can increase metal bioavailability in soil rhizosphere and therefore enhance metal accumulation capacity (Jiang et al., 2008). An improved metal accumulation shown by *H. annuus* due to the use of *B. aryabhattai* AB211 may have been via this mechanism.

Bacteria with ability to produce plant auxins, indole-3-acetic acid (IAA), siderophores and aminocyclopropane-1-carboxylate (ACC)) deaminase can potentially stimulate plant growth and enhance plant's ability to thrive under heavy metal toxicity and aid uptake of metals (Ma et al., 2011). The biosynthesis of IAA for example can occur via tryptophan-dependent or independent means. Bhattacharyya et al. (2017) reported that the strain AB211 synthesizes IAA with or without tryptophan, even though IAA was higher with tryptophan present. The authors also showed that the strain AB211 genome carries the required components for the synthesis of 3-hydroxy-2-butanone (acetoin) and 2,3-butanediol which has been reported to promote plant growth when synthesized by *B. subtilis* and *B. amyloliquefaciens* (Ryu et al., 2003).

Another means by which *B. aryabhattai* AB211 may have stimulated *H. annuus* growth and subsequent improvement of metal accumulation in our study is via the provision of soluble phosphates to plants. Even though phosphate is very abundant in the environment, they mostly exist in insoluble forms that cannot be used by plants. In the same vein, phosphate is one important nutrient that limits plant growth when unavailable or not in the required soluble quantity. Some bacteria have the capacity to solubilize insoluble phosphates by producing phosphatases or acidic metabolites (Hilda and Fraga, 1999). Lee et al. (2012) measured the solubilization of insoluble tricalcium phosphate by rhizobacteria, and *B. aryabhattai* showed high levels of soluble phosphates at levels of up to 676.8mg/L which may have contributed to the improvement in growth performance of *Xanthium italicum* in their microcosm study.

A growth promoting and metal accumulation effect on *H annuus* was observed for *B. aryabhattai* AB211, and this may be due to the production of soluble phosphates or may be due to the biosynthesis of IAAs or other beneficial phytohormones which have been reported as a plant growth promoting mechanism. In-depth studies into the content of the phytohormones is needed to ascertain the direct effects of bacterial inoculation. *B. aryabhattai* strains can be used as an environmentally beneficial means to revegetate barren lands but most importantly can be used to significantly improve the efficiency of phytoremediation in a sustainable way. Since it is a strain that has not been explored in significant detail in literature, more studies are encouraged using other plants to determine its usefulness in other environments and soil types.

(a) Control (left) alongside *B. aryabhattai (right)*

(b) Cd effects with (right) and without (left) *B. aryabhattai*

(c) Pb effects with (right) and without (left) *B. aryabhattai* AB211

(d) Zn effects with (right) and without (left) *B. aryabhattai* AB211

(e) Cd+Pb+Zn effects with (right) and without (left) *B. aryabhattai* AB211

Figure 5. 3 (a-e). Pictorial view of benchtop plants under different metal treatments with and without *B. aryabhattai* AB211 strains.

5.4 Conclusion

A greenhouse-based phytoremediation study was carried out to assess the metal uptake and biomass production capacity of sunflower especially when inoculated with a plant growth promoting bacteria. Study showed that the effect of heavy metals on *H. annuus* growth varies with metal types as *H. annuus* plants were significantly more tolerant to Zn and Pb than to Cd (which shows deleterious effects on plant growth and biomass yield). Even though sunflower showed good biomass productivity and metal uptake, the inoculation with *B. aryabhattai* AB211 enhanced its biomass yield and improved metal uptake and tolerance enabling the plant to attain hyperaccumulator status.

While risk management based phytoextraction is important, seeking ways to enhance biomass productivity for bioenergy using relatively safe biological inoculum is a key phytomanagement strategy for attaining added value from the process.

CHAPTER SIX

VALORIZATION OF POST-REMEDIATION BIOMASS: THE ROLE OF BIOCHARS IN MANAGING CONTAMINANTS IN AQUEOUS SOLUTION

6.1 Introduction

As mentioned in chapter one, direct or indirect exposure of the biota to toxic contaminants poses serious risks to humans and their immediate environment. Unfortunately, the prevalence of contaminants occurs at unacceptable levels worldwide (Raikova et al., 2019). More acceptable and environmentally friendly ways of disposing these contaminants are continually being sought. While research efforts seeking new ways constantly to engineer natural remediation, in-situ options involving adding amendments to soils to bind pollutants and provide conditions favourable to plant growth and ecological restoration are also being explored and gaining traction (Hoang et al., 2021; Qadir et al., 2022). Also gaining prominence in recent remediation discourse is the need to manage organic and inorganic pollutant effects in aqueous solutions (Ahmad et al., 2014). A key factor when evaluating pollutant risks to the environment is their bioavailability and mobility and this constitutes one of the most important considerations for regulators (Swartjes, 1999). There is less interest in total concentration of contaminants and more about the effect of the contaminant and this approach is referred to as the risk-based approach (Fernández, et al., 2005). Efforts aimed at reducing the effects of pollutants on the environment should be centred around addressing their bioavailability and mobility alongside reducing their total concentration.

As in phytostabilization as discussed in section 2.4.5.2.1, the amendment of soils as a remediation strategy aims to reduce associated pollutant transfer risks to receptor water bodies or organisms. Organic materials are a common choice for these types of amendments and are mostly derived from biological resource with little to no need for any kind of pre-treatment to soils. The use of amendments in soils could also serve as a veritable route for disposing off organic waste residues (e.g., anaerobic digester residues) no longer required for primary use. Activated carbon have been in used in soils and sediments as a remediation material because of its ability to reduce the bioavailability of contaminants and the associated risks (Yang et al., 2021a; Yang et al., 2021b). Activated carbons are carbonaceous materials made from the incomplete combustion of organic matter, followed by an activation phase to increase its surface area (Yang et al., 2021b). Organic contaminants (which are a mainstay in contaminated sites) have been reported to sorb well to surfaces of carbonaceous materials. Some of these are soot (Jonker and Koelmans, 2002), coal (Cornelissen & Gustafsson), and coke (Ghosh et al., 2003). Lower accumulation of contaminants in soils can be expected due to sorption caused by carbonaceous matter which is two times the sorption capacity expected from natural organic matter (Cornelissen et al., 2005; Kreitinger et al., 2007). Due to their huge sorption potential when present in contaminated sites, more deliberate efforts have been made to introduce cleaner types of these carbonaceous fractions (e.g., biochars, activated carbon) into soils and sediments to reduce the bioavailability of organic contaminants (Yu et al., 2019). For inorganic contaminants like heavy metals, reported instances of significant immobilization of heavy metals within soil matrices have been reported (He et al., 2019; Wang et al., 2020). In instances of dealing with sites involving both organic and inorganic pollutants, amendments with capacity to reduce the mobility and bioavailability of both organic and inorganic contaminants could present a cost-effective strategic advantage.

Removal of important heavy metals like Cd, Cr, Cu, Hg, Ni, and Pb are receiving increasing attention because of the associated negative effects they can potentially cause the environment. Zhou et al. (2013), using batch sorption experiments reported positive removal efficiency of Cd, Cu, and Pb by biochar modified by chitosan. Biochar produced from malt spent rootlets were also used to remove Hg(II) from wastewater, attaining favourable removal efficiency of up to 100% over a 24hr contact period (Boutsika et al., 2014). Manariotis et al. (2015) also reported a 6-fold higher sorption efficiency of Hg for malt spent rootlets biochars when compared to the raw materials. Using a developed $ZnCl_2$ modified glue residue biochar, Shi et al. (2020) achieved a maximum Cr(VI) sorption capacity of 325.5 mg/g.

Despite a myriad of published work on the removal of varieties of environmental contaminants using biochars, its application as a sorbent for treatment of heavy-metal-containing wastewater is still considered emerging and underdeveloped (Ahmad et al., 2014). On a review on the recent advances in biochar application for water and wastewater treatment, Wang et al. (2020) observed that most research on adsorption in aqueous solution focuses on single contamination even though actual prevailing realities involve varieties of co-contaminants. It is expected that adsorption should be lower in competitive aquatic systems (Harter et al., 1992). There have been reports of studies involving competitive sorption of heavy metals involving different types of sorbents ranging from zeolite (Shaheen et al., 2012), goethite (Zhu et al., 2012) palygorskite and sepiolite (Sheikhhosseini et al., 2013) water hyacinth (Zheng et al., 2016), etc. Very few of these studies have explored competitive sorption dynamics using biochar and there have been no report of the use of metal-rich biochar from sunflower derived from a phytoremediation process as an adsorbent in aqueous settings. Results in Chapter 5 of this thesis has demonstrated that sunflower plant is a good accumulator of heavy metals, and it is important to examine their suitability as surfaces for adsorption of more heavy metal contaminants when charred via pyrolysis. The aim of the work reported in this chapter is to assess the effectiveness of pyrolysis as a tool for bioenergy generation and biochars, to evaluate biochar as a medium for stabilizing accumulated contaminants and their potential use for wastewater treatments by exploring their adsorption behaviour in mono and multi-metal conditions in aqueous solution.

6.2 Results and discussions

6.2.1 Heating value of sunflower under different metal treatments

Biomass calorific value gives an indication of the chemically bound energy stored in biomass and during the combustion process, it is converted and releases heat energy. It has been considered as one of the most important indicators of the energy value of a fuel (Erol et al., 2010). The calorific value of sunflower under different metal treatments are shown in Table 6.1. The presence of metals in plant tissues does not appear to make a difference in the amount of the heating output. The calorific values ranged from 17.009 to 18.035 MJ/kg with the control having the highest heating value at 18.035% but this difference was not statistically significant ($p>0.05$). Recorded calorific value of some important plant-based biomass are *Phragmites australis* (17.933 MJ/kg), Typha augustifolia (18.117 MJ/kg), poplar (19.371 MJ/kg) (Gravalos et al., 2010). Others include silvergrass 17.4 MJ/kg (Wang et al., 2021c), switchgrass (17.48 MJ/kg) (Zhuo et al., 2015) and willow (19.59 MJ/kg) (Labrecque et al., 1997). In contrast, the calorific value of coal is around 25 – 35 MJ/kg, natural gas (53 MJ/kg), and crude oil 42.3 MJ/kg (Gaur & Reed, 2020). While these traditional energy sources have higher calorific value, they are mostly non-renewable and the processes involved in exploiting and utilizing them are unpleasant to the environment.

Table 6. 1. Heating values of sunflower under different treatments

Treatments	Calorific value (MJ/kg) (Mean $\pm$ SD)
Control	18.035 $\pm$ 0.08
Cd	17.009 $\pm$ 0.19
Pb	17.853 $\pm$ 0.46
Zn	18.004 $\pm$ 0.25
Cd+Pb+Zn	17.276 $\pm$ 0.50
AB211	18.018 $\pm$ 0.19
Cd+AB211	17.324 $\pm$ 0.50
Pb+AB211	17.439 $\pm$ 0.615
Zn+AB211	17.313 $\pm$ 0.40
Cd+Pb+Zn+AB211	17.390 $\pm$ 0.58

6.2.2 Pyrolysis yield

As shown in Table 6.2, the conversion of sunflower biomass to biochar at 500 °C was high at 51.6%. Yield value is higher than previously reported for sunflower straw pyrolyzed at 500 °C (He et al., 2016; Yue et al., 2018; Zhou et al., 2020). It has long been established that the characteristics of biochars are very dependent on pyrolysis temperature and residence time (Ahmad et al., 2014). Slow pyrolysis with a 2-hr run time was used because of its potential to yield more biochar product than fast pyrolysis (Yang et al., 2019), and the biochar yield obtained in this study confirms this. It is expected however that this yield will begin to decline with further increase in temperature (Gong et al., 2018; Zhou et al., 2020), possibly linked to volatilization and dehydration reactions, and lignocellulosic mass decomposition that occurs via the pyrolysis process (Kan et al., 2014).

Bio-oil yield was estimated at 22.3 % with syngas yield at 11.8 %, significantly below biochar yield. Slow pyrolysis favours char production over bio-oil or syngas (Yang et al., 2019). Lieven et al. (2008) reported that when metal-rich sunflower biochar was pyrolyzed at 400 °C, 500 °C, and 600 °C, no Pb, Zn was found in bio-oil and syngas fraction as they were all deposited in char fraction.

Table 6. 2. Pyrolysis yield of metal-rich sunflower

Pyrolysis temp (°C)	Char yield (wt %)	Bio oil yield (wt %)	Gas yield (wt %)
500	51.6	22.3	11.8

6.2.3 Characterization

Sunflower biochar properties are summarized in Table 6.3. The biochar was alkaline with pH at 10.48, and this is possibly linked to high temperature degradation of the organic contents of the biomass which releases alkali salts and can cause loss of acidic functional groups (Chen et al., 2011; Bandara et al., 2017). Elemental analysis for carbon, hydrogen, nitrogen, and oxygen (CHNO) was not carried out in laboratory due to unavailability of elemental analyser, which is a limitation of the work. However, CHNO data for sunflower biochar pyrolyzed at 500 °C was pooled from the literature. CHNO values of 66.7, 2.4, 0.8 and 12.2 % respectively was reported by Yue et al. (2018). CHNO values of 70.26, 4.47, 1.29 and 22.82% were reported by (Colantoni et al., 2016) and CHNO values of 78.99, 3.43, 0.64 and 16.87 % reported by Sun et al. (2019).

Table 6. 3. Sunflower biochar properties

	C (%)	H (%)	N (%)	O (%)	pH
Sunflower biochar	66.7 – 78.99	2.4 – 4.47	0.64 – 1.29	12.2 – 22.82	10.48

6.2.2 Total heavy metal concentration in sunflower-derived biochar after pyrolysis

The concentrations of cadmium, lead, and zinc in sunflower plant residue and its biochars pyrolyzed at 500 °C is shown in Table 6.4. After pyrolysis at 500 °C, the concentrations of metals increased significantly ($p<0.05$) in biochar except for Cd. The processes involved in biomass pyrolysis is complex with multiple sets of chemical reactions. Heavy metal migration from biomass phase to biochar phase during pyrolysis is a major cause of concern. Higher metal concentrations in biochar after pyrolysis has also been reported by Gong et al. (2018), and this is directly due to the reduced mass of biochar yield when converted from biomass. However, the decreased Cd concentration due to pyrolysis can be attributed to volatility. Kistler et al. (1987) once reported Cd reduction to Cd^0 for Cd existing as carbonates in raw materials when exposed to high temperatures and they were volatilized to the off-gas.

Table 6. 4. Heavy metal concentrations (mean ± SD) of sunflower biomass and its derived biochar at set pyrolysis process parameters.

	Cd (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
SBM	4.83 ± 2.46 a	70.78 ± 14.17 b	125.84 ± 21.63 b
SBC at 500 °C	2.93 ± 1.15 a	101.25 ± 15.13 a	179.56 ± 34.07 a

SBM: Sunflower biomass, SBC: Sunflower biochar, Cd: Cadmium, Pb: Lead, Zn: Zinc. Different letters within column indicates significant difference ($p<0.05$)

6.2.3 Speciation of heavy metals in sunflower metal-enriched biochar after pyrolysis

The activity and toxicity of heavy metals in the environment are dependent on their chemical speciation, and this can be determined via a Community Bureau of Reference (BCR) sequential extraction procedure. The BCR fractionation results are shown in Table 6.5, revealing the heavy metal content of harvested sunflower biomass and its biochar in four fractions: acid extractable (F1), reducible (F2), oxidizable (F3), and residual (4) fraction (von Gunten et al., 2017). The toxicity and effectiveness of the heavy metal fractions are in the order F1>F2>F3>F4 (Huang & Yuan, 2018). The heavy metals present in the F1 and F2 fractions are more readily bioavailable and can be easily absorbed by plants, therefore their toxicity is more direct and effective. The F3 fraction are more subject to degradation and leaching especially when exposed to strong oxidation and acidic conditions, and even though they show some toxicity, their effectiveness is less concerning for the environment (Devi & Saroha, 2014). The F4 fractions is considered non-bioavailable and non-toxic as the metals contained in the residual solids are in their crystallized structures (Fuentes et al., 2008; Devi & Saroha, 2014). Table 6.4 shows the BCR fractionation data of sunflower biomass and the heavy metals in its biochar produced from pyrolysis at 500 °C. Results suggest that pyrolysis can potentially be beneficial for converting unstable toxic fractions into stable components, thereby dealing with the associated problems of heavy metal toxicity. Figure 6.1 shows the percentages of Cd, Pb and Zn in SBM and SBC. Apart from Pb (48.5%), more than 50% of Cd and Zn are in the bioavailable portions (F1+F2) of the sunflower biomass residue. This represents great risk for the environment if these residues are left in the field after a harvest. Placement of plant residues in field after harvest is a typical agricultural practice to recycle nutrients for crop plants, enhance organic matter substrate provisioning for microorganisms and act as spongy surface for rainwater, thus reducing the risk of erosion. A notable decrease was observed in metals present in the bioavailable fractions when the plant residues were converted via pyrolysis into biochar. With the temperature at 500 °C, the percentage of bioavailable portions (F1+F2) declined, and consequently, there was a marked and stable increase in the percentage of metals in the residual portion (F4). Similar observations have been reported in previous studies (Jin et al., 2017; Zhou et al., 2020; Wang et al., 2021). These dynamics can easily swing with increase or decrease in pyrolysis temperature. It is expected that at higher temperatures, there will be adequate energy to break associated bonds, thus settling the heavy metals in the F4 zone. At lower temperatures, the energy may not be enough to attain the boiling point of heavy metals, making them less volatile and less likely to convert the F3 fraction to F4 (Zhang et al., 2018). However, at most pyrolysis temperatures used, an observed trend in most studies is that when biomass is converted to biochar through pyrolysis, there is a marked deportment of metals to the stable, non-toxic fractions (Wang et al., 2021). This is because with increased pyrolysis temperature, heavy metals favour a combination with biomass matter to form stable fractions in biochar (Chen et al., 2015). The properties of heavy metals can also contribute to the variations in fraction placement as some metals are more volatile than others (Liu et al., 2015). Cd and Zn are categorized as medium-volatility heavy metals (Liu et al., 2015). Also, the total metal concentration increased in biochar when compared to the biomass due to the reduction in volume during pyrolysis (Gherghel et al., 2019). Summarily, the current research has shown that pyrolysis sufficiently stabilizes heavy metal concentrations in pyrolysis residue, thus alleviating environmental risks but the extent is dependent on the heavy metal properties and the pyrolysis process parameters.

Table 6. 5. The speciation of heavy metals (mg/kg) in sunflower biomass and its derived biochar at set pyrolysis process parameters

	Cd (mg/kg)		Pb (mg/kg)		Zn (mg/kg)	
	SBM	SBC	SBM	SBC	SBM	SBC
F1	1.36	0.17	23.82	8.02	38.43	21.27
F2	1.27	0.26	16.11	12.50	21.38	30.13
F3	1.25	1.20	15.05	45.76	19.67	62.82
F4	1.29	1.45	27.36	50.39	19.68	81.17

SBM: Sunflower biomass, SBC: Sunflower biochar Cd: Cadmium, Pb: Lead, Zn: Zinc.

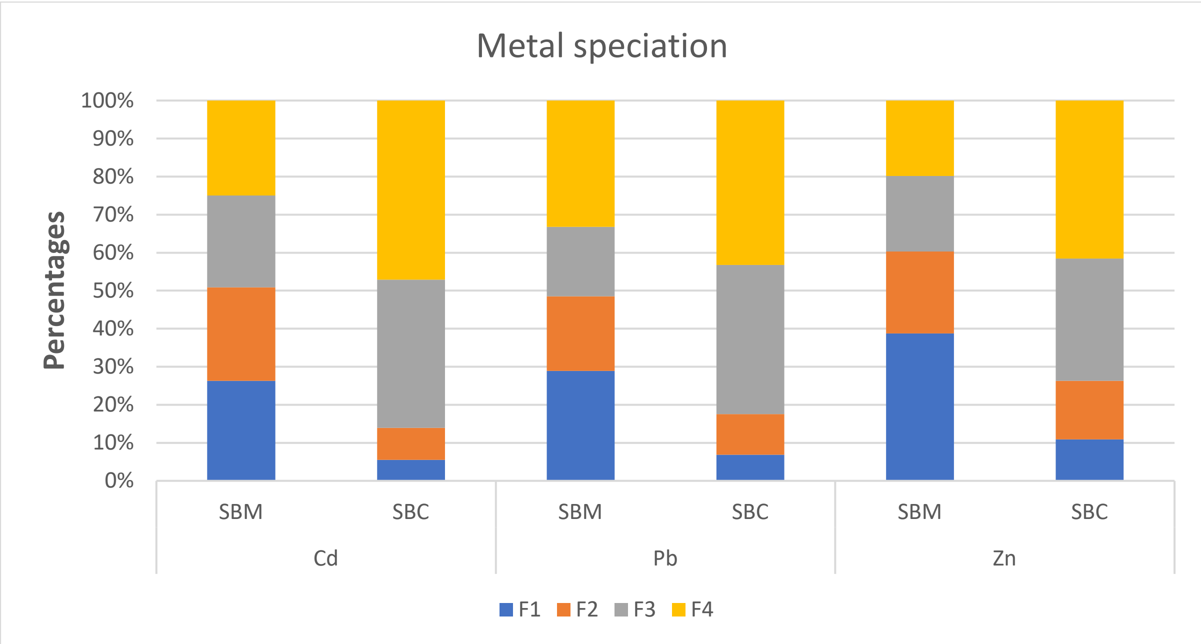
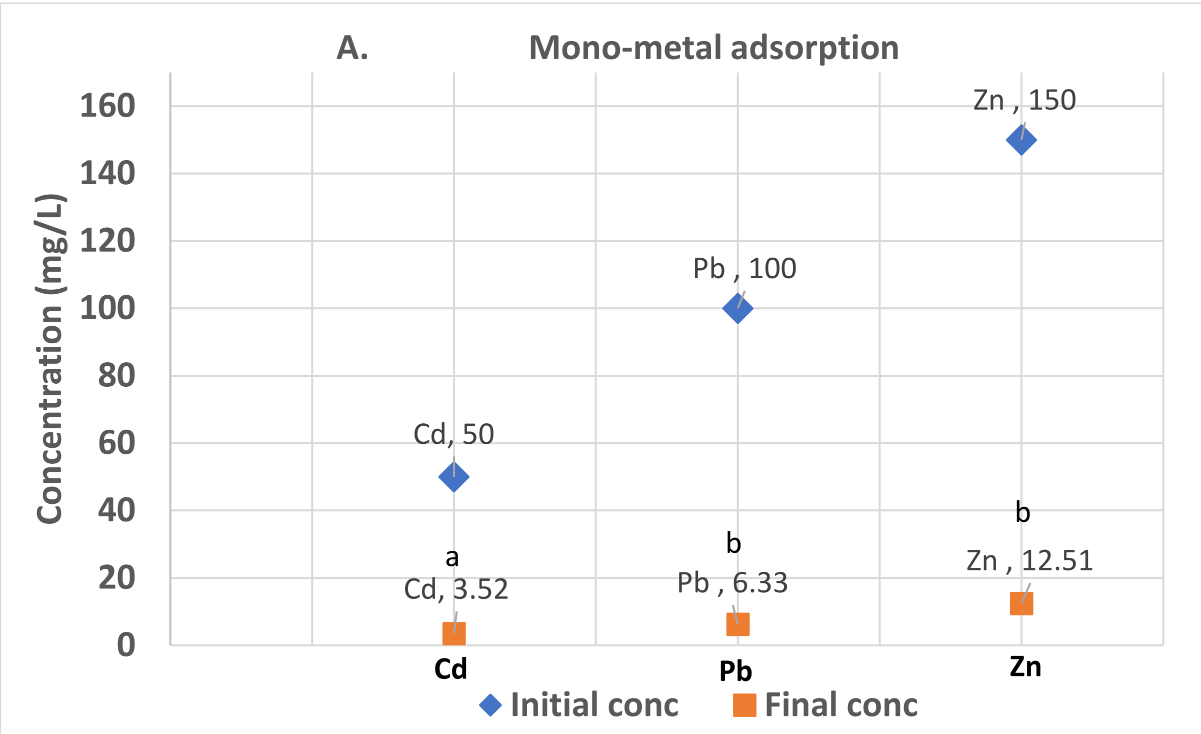


Figure 6. 1 Percentages of fractions of heavy metals in SBM and SBC. Cd: cadmium, Pb: lead, Zn: zinc, SBM: sunflower biomass, SBC: sunflower biochar.

6.3 Column adsorption of metal contaminants using sunflower-derived metal-enriched biochar

As indicated in Figure 6.1, initial concentration of the metals in aqueous solution was set at 50, 100 and 150 mg/L for Cd^{2+}, Pb^{2+} and Zn^{2+} respectively. Following adsorption via downward stream in column, there was a significant decrease in Cd^{2+} (92.96%), Pb^{2+} (93.67%) and Zn^{2+} (91.66%) concentrations for mono-metal adsorption, but less effective for multi-metal conditions (Cd 88.1%, Pb^{2+} 81.83%, and Zn^{2+} 81%). There was no difference in the adsorption rates within the treatments under mono-metal conditions, but for multi-metal conditions, Cd^{2+} removal rates were higher than Pb^{2+} and Zn^{2+}. This is possibly due to it having a lower concentration level (50 mg/kg). At low concentrations, metal ions can be easily adsorbed on to the surface of the biochar but with an increase in metal contaminants, biochar adsorption sites are more readily occupied, and this could reduce removal rates (Ni et al., 2019). Across mono-metal conditions, removal rates were in this order: $Pb^{2+} > Cd^{2+} > Zn^{2+}$, but under multi-metal conditions, removal rates were $Cd^{2+} > Pb^{2+} > Zn^{2+}$ (See isotherm study in Section 6.4 for further explanations). There was no effect of competitive adsorption on Cd^{2+} treatments. Even though there was a significant effect of competitive adsorption on removal rates for Pb^{2+} and Zn^{2+} treatments ($p<0.05$), removal rates were still high for multi-metal treatments and the deduction is that stable metal-enriched biochar was effective in the removal of heavy metals from aqueous solution.



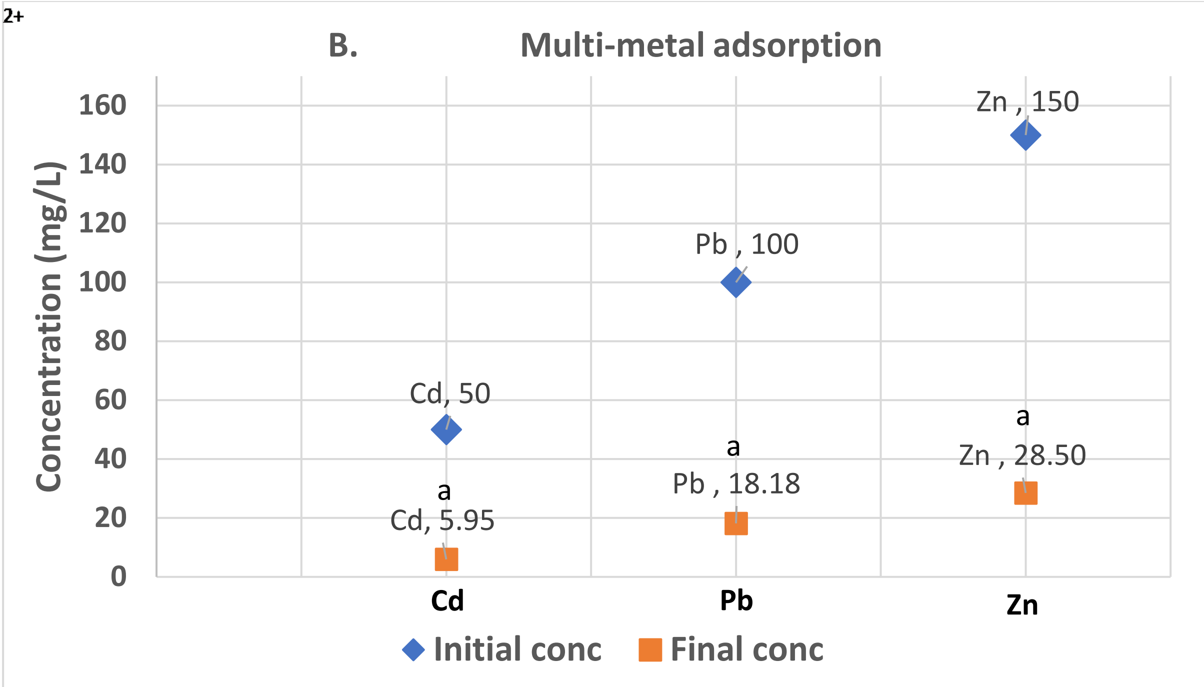


Figure 6. 2. Adsorption of Cd^{2+}, Pb^{2+} and Zn^{2+} using sunflower straw biochar in (a) Mono-metal and (b) multi-metal conditions. The y-axis shows the concentration of the different metals under consideration, the x-axis shows the metal type. Different letters between mono- and multi-metal treatments indicates significant difference ($p<0.05$).

6.4 Batch adsorption isotherms

Adsorption isotherms describes the relationships and interactions between adsorbates and adsorbents at equilibrium where temperature remains constant and are essential to adequately understanding adsorption processes (Ayawei et al., 2017). To understand the mechanism and predict the dynamics of adsorption systems, experimental data from adsorption experiments are modelled via adsorption isotherms and the most frequently used ones are the Langmuir and Freundlich models (Kalam et al., 2021).

The Langmuir model is a monolayer model that assumes that there are no mutual interactions between adsorbed molecules and each adsorption site has equal adsorption energy at constant temperature

The Langmuir model can be expressed in the linear form thus:

$\frac{Ce}{Qe} = \frac{1}{QmKl} + \frac{Ce}{Qm}$ ……………………………………………Equation 6.1

Where:

C_e is the concentration of adsorbate at equilibrium after adsorption (mg/L)

Q_e is the adsorption capacity of the adsorbent (mg/g) at equilibrium

Q_m is the maximum adsorption capacity of the adsorbent

K_L is a Langmuir constant that relates to adsorption capacity mg/g as it describes the strength of the interaction between adsorbate and adsorbent surface.

R_L is a dimensionless constant called the separation factor. It is defined mathematically as

$Rl = \frac{1}{(1+KlCo)}$……………………………………………Equation 6.2

Co is initial concentration of adsorbate.

Adsorption is favourable when $0 < R_L < 1$

The results in the isotherm data in Fig 6.3 seem to follow the shape of the Langmuir model, suggesting the pollutants are absorbed onto homogenous surface by forming a monolayer. The separation values shown in Table 6.6 indicates that the adsorption of Cd^{2+}, Pb^{2+} and Zn^{2+} were all favourable for the metal concentration range adopted. The high correlation coefficient R also shows good fit.

The Langmuir-type behaviour of biochar have also been demonstrated by Dewage et al. (2018) where they used pinewood-derived fast pyrolysis biochar in batch and fixed-bed studies to remove Pb^{2+} from wastewater. Using biochars derived from anaerobically digested sludge, Ni et al. (2019) explored the competitive behaviour of coexisting Pb^{2+} and Cd^{2+} in contaminated wastewater systems and reported a Langmuir-type adsorption isotherm pattern with Pb^{2+} having greater affinity to adsorption sites than Cd^{2+}. The Langmuir isotherm has been reported to be the best fit for heavy metal and anionic contaminants while the Freundlich isotherm fits better for organic contaminants (Ahmed et al., 2016). In a study reviewing biochar-based adsorbents and lignin-based adsorbents for wastewater treatment including their source, preparation methods and biochar behaviour, Sun et al. (2021) also concluded that the Langmuir model fits better to adsorption isotherm of heavy metals and anionic contaminants with the pseudo-second-order model fitting better for the sorption kinetics of all other contaminants.

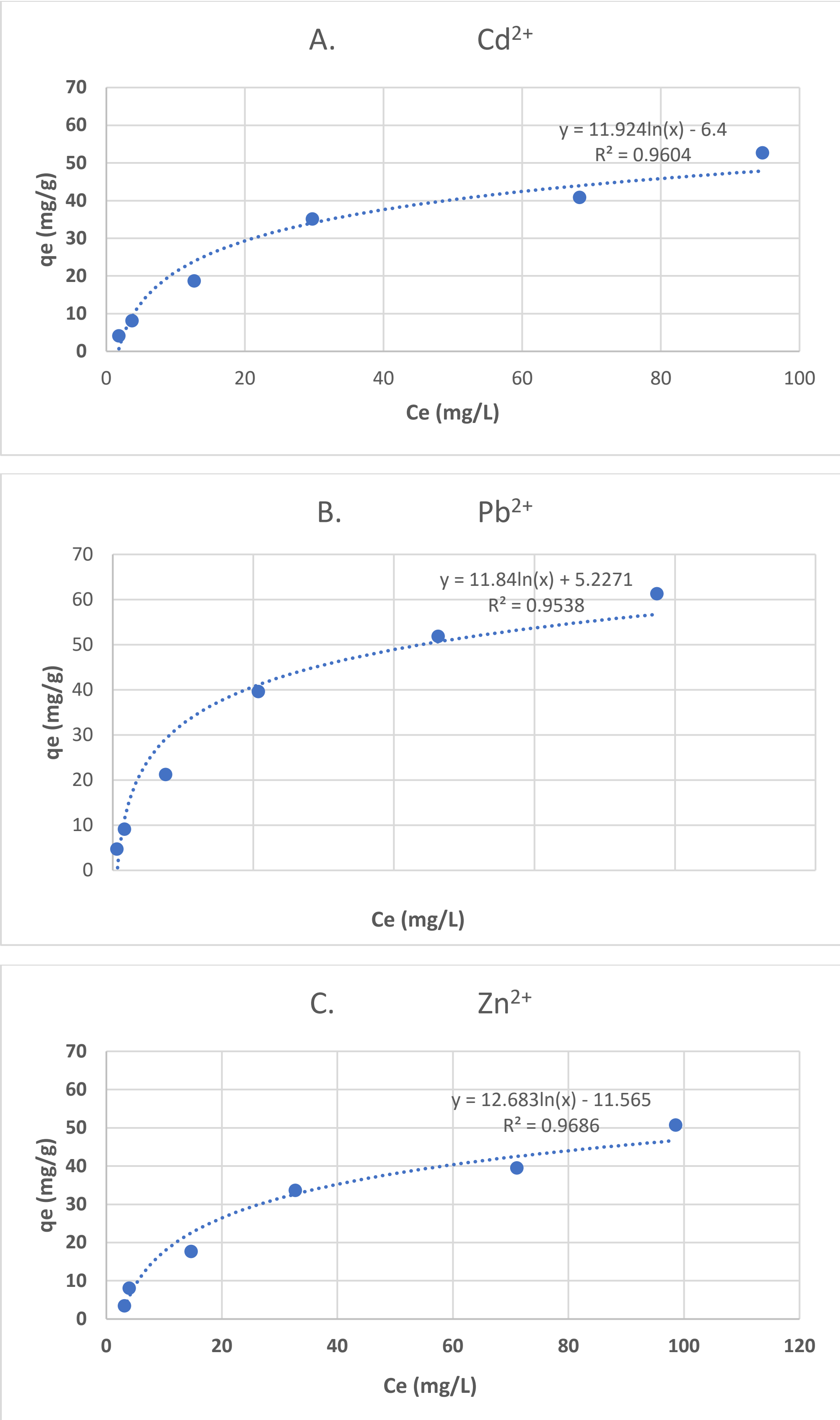


Figure 6. 3. Multimetal adsorption isotherm adsorption isotherms for (a) cadmium, (b) lead, (c) zinc by sunflower biochar in batch experiment. Y axis (qe): metal concentration adsorbed onto biochar, X axis (Ce): Metal equilibrium concentration in aqueous solution.

Table 6. 6. Langmuir model parameters for sunflower biochar

	Q_{max} (mg/g)	K_L	R_L	R^2
Cd^{2+}	60.44	0.0404	0.3308	0.9608
Pb^{2+}	57.07	0.2026	0.0899	0.9538
Zn^{2+}	143.51	0.0096	0.6751	0.9686

The competitive adsorption of Cd^{2+}, Pb^{2+} and Zn^{2+} onto sunflower biochars with initial concentration ranging from 10 to 200 mg/L are shown in Figure 6.3. the equilibrium adsorption capacity of the sorbent increased with increasing adsorbate concentration at equilibrium. As with the column experiments, the order of metal adsorption by biochar is $Pb^{2+} > Cd^{2+} > Zn^{2+}$. This is confirmed by the K_L values in Table 6.6 which gives an indication of the strength or the extent to which metal ions binds on to the adsorbent surface. K_L as an index indicates potential mobility of metals. With stronger sorption to adsorbent, solubility is expected to be lower (Park et al., 2016). Pb^{2+} has the highest K_L value suggesting a strong affinity to biochar surface. Park et al. (2016) also suggested that Pb^{2+}'s hydrated radius smaller than Zn^{2+} and Cd^{2+} and has higher affinity to most functional groups in organic matter (phenolic and carboxylic groups inclusive). Greater affinity of Pb^{2+} on biochar over Zn^{2+} and Cd^{2+} has also been reported in previous studies (Soria et al., 2020; Yang et al., 2021a). Wu et al. (2019) reported that the alkalinity of the biochars may facilitate its removal by the formation of a Pb^{2+} ion precipitate. However, the Q_{max} value for Zn^{2+} is higher as shown in Table 6.6 indicating greater maximum capacity of adsorbent for Zn^{2+}. Results from column and batch studies illustrates the biochar's preference to Pb^{2+} surface over Cd^{2+} and $Zn^{2+.}$ Similar order of preference was also reported by Xue et al. (2012) using fixed bed columns of biochar for the removal of a variety of heavy metals (Pb^{2+}, Cd^{2+} and Ni^{2+}). Their result showed the column's capacity to remove heavy metals in the order $Pb^{2+}>Cd^{2+}>Ni^{2+}$. Overall, sunflower biochar exhibited very good potential to remove these metal ions even though at varying degrees.

6.5 Conclusion

Post-remediation metal-enriched sunflower biomass was slowly pyrolyzed to derive valuable metal-rich biochar and this biochar was explored as an adsorbent for the removal of heavy metal contaminants from wastewater. A BCR sequential extraction procedure showed reduced bioavailability of metals after pyrolysis indicating reduced risks of heavy metal contamination when utilizing the derived biochar. In the multi-metal system, post-pyrolysis biochar exhibited good heavy metal removal capacity as a sorbent in wastewater showing greater affinity to Pb than Cd and Zn and this relationship fits well to the Langmuir adsorption isotherm model. Reducing bioavailability is a key provision for a risk-based phytomanagement approach for mitigating the associated problems of toxic contaminants (Cundy et al., 2016). Additionally, biochar can potentially be modified to improve its adsorptive properties as it has been reported that modification of biochar-based adsorbents can result in increased adsorption capacity in relation to pristine biochar (Sun et al., 2021).

In the aftermath of its use as sorbents for wastewater treatment, biochar can potentially be used as material for soil amendments (Vilas-Boas et al., 2021). However, to further utilize or safely dispose used biochar, it is important to confirm lack of mobility of metals following application to soil via further sequential extraction procedure. In cases where metal remain mobile, encapsulating metals using cement-based solidification/stabilization procedures offers a relatively reduced-risk option of disposal of biochar loaded with heavy metal ions (Tejada-Tovar et al., 2022).

CHAPTER SEVEN

GENERAL DISCUSSION, LIMITATION/RECOMMENDATION AND CONCLUSION

Metal contamination is currently a global ubiquitous phenomenon, which makes it of great environmental concern since its persistence in nature is indefinite (Shen et al., 2021). Phytoextraction of metal contaminants utilizing energy crops to concentrate metals in the aboveground biomass is considered an environmentally friendly option for remediation (Rheay et al., 2021). This utilization of energy crops for phytoremediation is proposed to gain added value from the technology by deriving some valuable energy output via biomass valorization and reducing waste by utilizing by-products derived from the process, thus making the practice more sustainable and environmentally appealing. In addition, the application of plant growth promoting bacteria to accumulating energy plants used for phytoremediation potentially makes the process more effective (Kong et al., 2017).

This study examined the applicability of phytoremediation (using sunflower) as a sustainable biotechnology to remediate metal contaminated soil, generate bioenergy and treat wastewater using by-products obtained from the process. The major findings from this work are:

1. The study selected the most ideal species for coupling phytoremediation with bioenergy/biochar generation using a multicriteria decision matrix and sunflower and silvergrass emerged as the two top candidates.
2. Sunflower was largely effective in accumulating metal contaminants into its aboveground tissues, and this was enhanced by up to 19 – 37% by the application of plant growth promoting bacteria, *Bacillus aryabhattai,* AB211, even though the degree of success varies with the kind of metal contaminants.
3. Sunflower biomass valorization via pyrolysis generated up to 22.3% bio-oil yield, 51.6% biochar yield with metal stabilized in biochar fraction, not bioavailable to pose serious ecotoxicity risks.
4. Sunflower-derived biochar reduced the concentration of metal contaminants in aqueous solution by 91.66 – 93.67% in mono-metal conditions and 81 – 88.1% in multi-metals conditions in column studies.

In the following sections, the major findings listed above are expanded upon to make further inference and discuss their implications.

7.1 Summary of findings and discussion

7.1.1 Sunflower and silvergrass emerging in MCDM analysis of candidates and implications

A multicriteria analysis study was carried out to ascertain based on set criteria and key indicators, the most ideal plant species for coupling phytoremediation with bioenergy generation. Results revealed silvergrass and sunflower as the top performers based on data obtained from systematic review of the literature. These species performed well in most of the phytoremediation-based criteria and bioenergy-based criteria.

Bioenergy options are being explored as an alternative to fossil fuels, which currently caters for a significant portion of global energy demand, adding significant carbon dioxide pollution to the atmosphere. Countries have set up mandates to meet the International Energy Agency's goal to make biofuels meet about 27% of world transportation energy demand by 2050 (IEA, 2011). Mandates are typically developed around the need to support domestic energy needs, reducing fossil fuel dependence, and reducing associated emissions caused by the usage of fossil fuels. With phytoremediation being an explored option for metal contamination control given its environmental benefits, burgeoning questions about the sustainability of the practice persist. Bonding phytoremediation practice using energy crops is a sustainable way to generate some bioenergy resources along with achieving set phytoremediation objectives. To attain additional bioenergy benefits from phytoremediation, the species selected is one of the most crucial considerations to explore. Countries are currently exploring potential promising energy crops to meet their bioenergy demand quota and crops like *Jatropha, Castor* and *Miscanthus* have been considered (Pandey et al., 2016). There is however no established scientific systematic basis for these selections, especially when considering the enormity of the importance of these decisions. The study carried out for the first time, an across-board synthesis of global data on plant performance based on important phytoremediation and bioenergy criteria and aggregate them to find the ideal species for a synergy of both properties. From the study in chapter 4, silvergrass

(*Miscanthus*) and sunflower emerged as the top two candidates. Silvergrass is a rhizomatous perennial C4 grass plant that are propagated by seed or rhizome dispersal. They are a second-generation energy crop (Lewandowski et al., 2000), high yielding in biomass (Pidlisnyuk et al., 2014), tolerant to harsh environmental conditions (Chou, 2009), lignocellulosic (Han et al., 2011), high calorific value (Brosse et al., 2014), metal tolerant and pollutant accumulators (Pidlisnyuk et al., 2014). Sunflower on the other hand have good metal tolerance (Winska-Krysiak et al., 2015), are good contaminant accumulators (Ion et al., 2014), have high yielding lignocellulosic biomass (Nguyen et al., 2021) and are largely a second-generation crop (PFAF, 2019).

In linking these practices together, it is important that dedicated promising energy crops (such as silvergrass and sunflower) be planted on contaminated marginal lands for the extra benefit of aesthetics, carbon sequestration, substrate quality improvement and as a means of tackling the problem of limited agricultural land since cultivation will be on neglected polluted sites. The EU-sponsored REJUVENATE project highlighted the importance of utilizing energy crops on marginal land. Generating valuable energy-based biomass from these marginal lands using waste-derived organic matter as fertilizers for soil improvement and restoration provides an opportunity to attain sustainable resource development while attaining a variety of wider benefits, and also provide the added benefit of supporting the re-use of sites that are deemed 'hard to develop' (REJUVENATE, 2009). The EU-REJUVENATE project findings also indicated that there are still data gaps that requires further demonstration projects on the re-use of marginal lands for biomass production and maximization. These demonstration projects should consider diverse regional, technological, and economic aspects as it aims to validate findings from the decision support tools adopted during the project. Wider benefits can also be attained from the use of risk-based phytomanagement and other gentle remediation-based management strategies (GREENLAND, 2014). Some identified wider benefits (based on data from the GREENLAND and HOMBRE projects) are soil improvement (Evangelou et al., 2015), water resource improvement (ANL, 2008), provision of green spaces (ANL, 2008, Cundy et al., 2013), climate change mitigation (Witters et al., 2012; Cundy et al., 2013; GREENLAND, 2014), and other socio-economic benefits (Cundy et al., 2013; GREENLAND, 2014)

Also, silvergrass and sunflower are non-woody perennial crops with the advantage of fast growth and ease of cultivation. Prior large-scale phytoremediation work on contaminated lands have been focused on fast growing short-rotation woody plants (Volk et al., 2006; Liu et al., 2013). Achieving remediation goals at a faster pace with non-woody second-generation plants is of immense advantage to the technology.

7.1.2 Potential of Sunflower for phytoextraction

A pot experiment was carried out in chapter 5 to access the effect of metal contaminants on plant growth and metal accumulation of sunflower when elevated Cd (50 mg/kg), Pb (300 mg/kg) and Zn (600 mg/kg) concentrations were added to the soil. Results on dry weight of leaves, stems and roots showed that Cd and Cd+Pb+Zn were the most toxic on sunflower growth and development. Tolerance (dW of contaminated biomass/dW of control) on Zn (74.31%) were good even though concentrations applied were elevated and over the general phytotoxicity thresholds (EPA, 2007), tolerance on Pb was average (45.65%) and tolerance on Cd was poor (13.04%). However, sunflower accumulation for heavy metal (Cd, Pb and Zn) was generally good with its bioconcentration and translocation factors ranging from 0.81 – 0.94 indicating adequate suitability even though this places it below the hyperaccumulator threshold of 1.

Sunflower is a recognised as an important bioenergy crop as indicated by the study in chapter 4 and a host of other published work (Zabaniotou et al., 2008; Iram et al., 2019; Nguyen et al., 2021). Its high biomass production makes it a boon for sustainable conservation and bioenergy production efforts. The usability of sunflower for phytoremediation at field scales have also been tested. Nehnevajova et al. (2006) carried out a comparative assessment of 15 commercial sunflower cultivars to determine the most promising cultivar in terms of growth, metal extraction and accumulation. Results suggest Cultivar Salut performed best based on cumulative metal extraction from contaminated sites and importantly observed that there is negligible concentration of toxic metals on sunflower seeds and oils which makes its added value production crucial for post-harvest considerations and generally making the process more economically attractive. Herzig et al. (2014) also carried out a 5-year time series field based phytoextraction experiment using sunflower and tobacco to manage Zn contamination and concluded that phytoextraction treatment with sunflower lowered Zn pool in soils by about 45-70% when compared with non-treated sites.

For this study, even though sunflower performs considerably well as a heavy metal accumulator, it fell marginally off the qualitative hyperaccumulator status (BCF and TF > 1) and performs a lower than established hyperaccumulator plants such as *Thlaspi caerulescens* (Chaney et al., 2005), *Pteris viattata* and *Sedum plumbizincicola* (Li et al., 2018). It is therefore necessary to incorporate some agronomic practices (Singh & Pandey, 2013) and plant growth promoting microorganisms (Abhilash et al., 2016) to the technology to enhance the growth of plants, improve its resistance to diseases and abiotic stress factors, enhance its biomass and biofuel production and improve its remediation capacity.

7.1.3 Role of plant growth promoting bacteria, *Bacillus aryabhattai* on plant growth and implications for sustainable phytoremediation.

Toxicity caused by metal contaminants leads to decrease in plant growth (Zhang et al., 2015; Yadav et al., 2021), but some bacteria generally termed plant growth promoting bacteria (PGPBs) have been evidenced to limit heavy metal toxicity and ameliorate the associated toxic effects and thus improve plant growth (Sheng et al., 2012; Chen et al., 2013; Sansinenea, 2019). Also, PGPBs have also been reported to improve plants capacity to extract heavy metal contaminants from soils (Sheng et al., 2012; Ahemad, 2019). A pot experiment was carried out in chapter 5 to investigate the role of *B. aryabhattai* in enhancing phytoextraction of heavy metals up into the aboveground tissues of sunflower plants. Root inoculation with *B. aryabhattai* AB211 showed it to have growth promoting effects on sunflower, thus enhancing its phytoextraction efficiency. Pot experiment carried out demonstrated that the application of strain AB211 improved plant dry matter yield for sunflower when soils were amended by Pb and Zn but the effect on sunflower in soils amended with Cd was not significant ($p<0.05$). The effects on metal accumulation by sunflower showed enhancement efficiency ranging from 19 – 37% depending on the metal treatment. Root development was more profound in plants with bacterial strain than those without, which could be linked to its enhanced uptake capacity. Enhanced performance by sunflower inoculated with *B. aryabhattai AB211* could be linked to its ability to produce IAA and siderophores (Ullah et al., 2015) and phosphate solubilization (Lee et al., 2012). Considering the results elucidated in chapter 5, the potential utilization of *B. aryabhattai,* can be regarded as a viable means of enhancing plant growth and metal accumulation in plants, as well as reducing the toxic effects of heavy metals in sunflower and potentially other energy crops.

Biomass production is a key element of any energy production scheme. It has direct implication for bio-oil/biofuel production, biochar/ash production and indirect beneficial effects on phytoextraction. Plant growth promoting microorganisms (PGPMs) are a veritable asset for sustainable conservation due to their ability to support plant growth and consequently, biomass production by aiding its access to essential nutrients and ameliorating the effects of biotic and abiotic stresses on plant (Glick, 1995; Ahemad, 2019). In light of this, PGPMs could be exploited as a requisite mechanism for enhancing energy crop yield (and consequently valorization yields) in a sustainable way. However, despite their demonstrated success in hydroponic settings (Kong & Glick, 2017), application at field levels have not been adequately exploited towards enhancing energy crop biomass production and contaminant accumulation.

7.1.4 The effect of post-remediation pyrolysis of metal-rich sunflower biomass on the stabilization and immobilization of heavy metals.

Studies have suggested that pyrolysis has huge potential to stabilize and immobilize heavy metals contaminants in the pyrolysis products, hence mitigating the release of toxic metal contaminants to the environment (Xiao et al., 2015; Niu et al., 2017). A slow pyrolysis procedure was carried out in Chapter 6 of this report to convert post-remediation, metal-rich sunflower biomass to biochar. The biochar products were then analysed via BCR sequential extraction to understand the compartmentalization dynamics in biochar solid fractions. Summarily, results showed that pyrolysis was efficient in settling heavy metals in non-bioavailable residual fractions when pyrolyzed at 500 °C even though results can vary with varying process parameters and the characteristics of the heavy metals in question plays a crucial role in these dynamics.

Given the advantages of phytoextraction already explored in this report, it also presents a challenge of dealing with the metal-rich biomass generated from the process which is a major limiting aspect of the technology. Biomass reutilization comes with great risks of secondary pollution to soil and water bodies. A thermochemical conversion gives the advantage of reducing the volume of contaminated biomass and possible stabilization of metals in biochar residual fractions. Pyrolysis of post-remediation sunflower biomass as demonstrated in this report shows promise as heavy metals were successfully stabilized in non-toxic fractions to a reasonable degree. This opens possibilities for these biochars to be re-utilized as soil amendments at reduced risks to the environment and a means to safely dispose of biochar wastes where necessary with little environmental consequence. Also, bio-oil and syngas yield were estimated at 22.3 % and 11.8 % respectively of biomass weight and it has been demonstrated that when metal-rich sunflower biochar is pyrolyzed, metals are not transferred to bio-oil and syngas fraction as they all deposited in char fraction (Lievens et al., 2008). This is especially important as sustainability efforts are tailored towards preventing secondary pollutions to the environment. Achieving post-phytoextraction derived bio-oil free from metal contaminants presents an avenue to meet alternative energy demand targets and help foster a bio-based economy geared towards achieving sustainable development.

However, there have been reports of the economic costs of operating pyrolysis-based remediation systems (Xiao et al., 2018; Robb et al., 2020), very little effort has been put towards quantifying the environmental benefits against economic costs. Environmental benefits like ecosystem goods and services, vegetation cover, remediated water and soils are hard to quantify. Also, adopting in-situ biochar production and utilizing feedstock from remediation processes reduces transportation costs and curtails the overall cost estimate of running the operation.

7.1.5. The effectiveness of stable metal-rich sunflower biochar for heavy metal removal in aqueous solution and implications for wastewater management.

Sunflower-derived metal rich biochars generated from the pyrolysis process were used as biosorbents to further remove heavy metal contaminants from aqueous solution. A column experiment and a batch adsorption experiment were used to ascertain the feasibility of utilizing already contaminated biochar to further sorb metal contaminants in water and an adsorption isotherm was used to model experimental data. Results showed that sunflower derived sorbents adequately removed metal contaminants in this manner: Pb > Cd > Zn for both column and batch adsorption experiments and the Langmuir isotherm model shows high correlation coefficient R^2 (0.9538 – 0.9686) for the three metals, indicating a good fit and the K_L values indicates a strong interaction between adsorbent and adsorbate for Pb but less so for Zn. Data seems to follow the shape of the Langmuir model, suggesting the pollutants are absorbed onto homogenous surface by forming a monolayer. Overall, results suggest these biosorbents are effective for heavy metal removal in aqueous solution.

The low cost of plant-based feedstock (especially when obtained as wastes from phytoremediation), the relatively simple preparation process and its favourable physicochemical properties makes the use of biochars desirable and feasible for application as sorbents for wastewater treatment. The research showed sunflower biochar made under documented optimal condition to successfully sorb metal contaminants. Biochars capacity to sorb contaminants are directly linked to important physicochemical properties relating to feedstock type, the nature of the thermal conversion process and the conditions of preparation, which suggests that its adsorption capacity can be improved via some sets of modifications (Zhang et al., 2020). Biochar modification via chemical and physical activation methods have been demonstrated to alter functional groups on biochar surfaces in ways where its porous structures and surface area is enhanced, thus increasing its surface oxygen containing group (Enaime et al., 2020). Biochars are unique and versatile and given that they can also be effective even when enriched with metal contaminants, they present an opportunity for managing biowastes while tackling a wide array of environmentally concerning contaminants. Continual in-situ experiments using different feedstock types, with different modification trials on real effluents should be encouraged to understand how these biochars function in the environment as researchers traverse towards transitioning into larger scale applications.

7.2 Limitations and recommendation

In the first phase of the study (chapter 4) where suitability data were aggregated from various sources globally, multiple factors that may have influenced data collected were not accounted for in the analysis. For example, when evaluating growth rate, performance in tropical and temperate region may differ for certain species. Multicriteria tools are better suited when applied to defined conditions and locations and should be applied thus.

Phytoremediation studies were carried out in greenhouse, using pots and other greenhouse equipment and very subject to controlled conditions. Real-world realities are different and transitioning of advanced phytoremediation technology from laboratory to field is still struggling with implementation (Saxena et al., 2019). Information from long-term field studies are critical to demonstrating the feasibility of these chains of technologies in managing the burgeoning environmental problems in the real-world. Whilst information from laboratory processes usually precedes its implementation in real-time, efforts should be made to test the feasibility of these processes at larger scales.

Adsorption experiments in this report were carried out using synthetic metal-contaminated water to account for competitive wastewater metal contamination. Real industrial wastewater effluents factoring in contributing components like colour, COD, BOD and other parameters should be considered in future research designs as these can play crucial role in understanding the adsorption capacity of biochars

Adsorption experiments were carried out at specified process parameters (documented to be optimal) due to the constraints associated with limited sunflower-derived biochars. Adsorption qualities of biochars are influenced by multiple factors such as pH, dose of biochar applied, contact time between biochar and adsorbate, and CEC (Dissanayake et al., 2020). Future work should centre around testing metal-rich sunflower biochar's adsorption capacity under varying physico-chemical conditions to ascertain its robustness and stability as bio-sorbents, as this is critical to the long-term application of this technology (Han et al., 2016).

Although studies have been carried out on the economy of phytoremediation, pyrolysis and adsorption technology, these studies are usually limited in scale, and are mostly done in isolation as separate processes. Detailed economical assessment of large-scale application of these technologies as a multifaceted unit is required to establish its application as a feasible alternative to environmentally destructive clean-up and energy production processes.

7.3 Conclusion

The study provides new insights into a multi-faceted approach to managing environmental contamination sustainably. It surveyed the feasibility of safe reutilization of by-products and wastes from remediation processes and explored avenues where added values can be obtained from the process. An in-depth multicriteria analysis was first undertaken to determine the most suitable species for a synergistic application of phytoremediation and bioenergy production technology. Silvergrass and sunflower emerged as the top performers. Sunflower was grown in greenhouse studies and showed good metal accumulating capacity, and this was enhanced by a plant growth promoting bacteria, *Bacillus aryabhattai*, indicating that plant growth promoting bacteria in combination with their plant host can influence growth, productivity, and tolerance to unfavourable conditions. Sunflower also showed excellent biochar yield when pyrolyzed, verifying the suitability of slow pyrolysis to achieving optimal biochar yield and the process of pyrolysis stabilized heavy metals in stable residual fractions in the biochar, thus making them reusable as soil amendments or as a surface for adsorption of contaminants from wastewater.

Phytoremediation offers a less intrusive and environmentally sustainable technology option for contaminant control and when combined with energy production, it opens opportunities to attain society's economic and environmental goals in a sustainable manner. An understanding of the complex interactions relating to contaminant variables, plant and microbe relationships, valorization technologies and waste management would make implementation convenient and seamless. A multidisciplinary approach incorporating diverse expertise from a wide range of fields is critical to achieving continual success.

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Appendix

1: Metal concentration in soil and H. annuus bioconcentration and translocation factors

Treatments	Spiked metal conc. in soil (mg/kg)	Actual metal conc. in soil on Day 0 (mg/kg)	Bioconcentration factor	Translocation factor
Control	----	----	----	----
Cd	50	46.96	0.83 ± 0.03	0.81 ± 0.03
Pb	300	288.22	0.88 ± 0.01	0.89 ± 0.10
Zn	600	568.70	0.85 ± 0.07	0.94 ± 0.04
AB211	----	----	----	----
Cd+AB211	50	47.46	1.31 ± 0.06	1.05 ± 0.03
Pb+AB211	300	279.49	1.16 ± 0.04	1.08 ± 0.04
Zn+AB211	600	544.15	1.15 ± 0.03	1.00 ± 0.02

2. Operating parameters of ICP-OES (iCAP 1600)

Operating parameters of the thermos ICP-OES (iCAP 1600)

Power (W)	1150
Auxiliary gas flow (L/min)	0.5
Nebuliser gas flow (L/min)	0.75
Coolant gas flow(L/min)	12
View	Axial
Purge gas flow	Normal
Flush pump rate (rpm)	100
Analysis pump rate (rpm)	50
Camera temperature	-47
Optics temperature	38

Wavelengths used on the ICP-OES of the elements investigated.

Elements	Wavelength (nm)
Cd	228.802
Cr	283.563
Cu	324.754
Fe	259.940
Mn	257.610
Ni	221.647
Pb	220.353

Sb	206.833
Zn	213.856

2. Conferences and accepted peer-reviewed publications

2.1 CEST, 2019

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COMBINING PHYTOREMEDIATION WITH BIOENERGY PRODUCTION: DEVELOPING A MULTI-CRITERIA DECISION MATRIX FOR PLANT SPECIES SELECTION

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Conference:
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Abstract:
COMBINING PHYTOREMEDIATION WITH BIOENERGY PRODUCTION: A MULTICRITERIA DECISION MATRIX FOR PLANT SPECIES SELECTION O.N. Amabogha. D. Purchase*. H. Garelick, H. Jones. Department of Natural Sciences, Faculty of Science and Technology, Middlesex University. The Burroughs London NW4 4BT United Kingdom. *Corresponding author: D.purchase@mdx.ac.uk Abstract The use of plants to extract heavy metal contaminants from soils has been proposed as a cost-effective means of remediation; and utilizing energy crops for this phytoextraction process is a useful way of attaining added value from the process. To simultaneously attain both these objectives successfully, the kind(s) of species selected is crucial. The species selected needs to satisfy certain important criteria including translocation index, metal and drought tolerance, fast growth rate, high lignocellulosic content, good biomass production, adequate calorific value, second generation attribute and a good rooting system. It is therefore necessary to develop a set of comprehensive selection criteria to select the most appropriate plant species suited to attaining the desired objectives. In this study, we used a systematic review approach to develop a multicriteria decision matrix for species selection. Eight species (sunflower, Indian mustard, soybean, willow, poplar, Typha, Miscanthus, switch grass) were selected on the basis of amount of hits on a number of scientific search databases. We identified the relevant criteria

2.2 ENVIRONMENTAL SCIENCE AND POLLUTION RESEARCH JOURNAL PUBLICATION

Environmental Science and Pollution Research

Combining phytoremediation with bioenergy production: Developing a multi-criteria decision matrix for plant species selection

--Manuscript Draft--

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Order of Authors Secondary Information:	
Funding Information:	Federal Ministry of Agriculture and Rural Development, Nigeria (NDDC/DEHSS/2016PGFS/BYS/PhD/007) — Mr Obed Nadari Amabogha
Abstract:	The use of plants to extract metal contaminants from soils has been proposed as a cost-effective means of remediation; and utilizing energy crops for this phytoextraction process is a useful way of attaining added value from the process. To simultaneously attain both these objectives successfully, selection of an appropriate plant species is crucial to satisfy a number of important criteria including translocation index, metal and drought tolerance, fast growth rate, high lignocellulosic content, good biomass production, adequate calorific value, second generation attribute and a good rooting system. In this study, we proposed a multi-criteria decision analysis (MCDA) to aid decision making on plant species based on information generated from a systematic review survey. Eight species Helianthus anuus (sunflower), Brassica juncea (Indian mustard), Glycine max (soybean), Salix spp. (willow), Populus spp. (poplar), Panicum virgatum (switchgrass), Typha latifolia (cattails), Miscanthus sinensis (silvergrass) were examined based on the amount of hits on a number of scientific search databases. The data was normalized by estimating their min-max values and their suitability. These criteria/indicators were weighted based on stipulated research objectives/priorities to form the basis of a final overall utility scoring. Using the MCDA, sunflower and silvergrass emerged as the top two candidates for both phytoremediation and bioenergy production. The multicriteria matrix scores assist the process of making decisions because they compile plant species options quantitatively for all relevant criteria and key performance indicators (KPIs) and its weighing process helps incorporate stakeholder priorities to the selection process.

3. Multicriteria decision matrix using z-score normalization

Criteria	Key indicator	Plant species								Weight
		Sunflower	Indian mustard	Soybean	Silvergrass	Poplar	Willow	Switch grass	Cattails	
Pollutant accumulation	Translocation index	0.28	0.43	1.88	-0.22	0.44	-0.48	-1.05	-1.28	0.15
Growth rate (Short rotation)	Crop growth rate (CGR)	-0.29	-0.47	-0.06	1.63	-0.98	-0.99	1.42	-0.25	0.30
Root system	Root depth	1.23	-1.19	-0.22	0.10	-0.06	0.42	1.23	-1.52	0.05
Metal tolerance	Metal tolerance index	-0.93	-1.05	-1.07	0.08	0.78	1.19	1.32	-0.32	0.10
Biochemical composition	Lignocellulosic biomass	1.28	-1.02	-0.88	-0.16	1.29	0.85	-1.00	-0.36	0.05
Biomass production (tons per acre)	Total dry biomass (matter) yield	2.04	-0.86	-0.25	0.44	-0.90	-0.92	0.02	0.43	0.25
Thermal energy potential	Calorific value in MJ per kg	0.07	0.06	-1.39	0.09	1.60	0.96	-1.25	-0.15	0.05
Drought tolerance	Drought tolerance index	0.71	0.91	0.70	0.40	0.19	-0.21	-0.55	-2.15	0.05
	Aggregate weighted scores	0.5635	-0.4585	-0.0050	0.5955	-0.224	-0.379	0.327	-0.4005	1

The cells in the matrix contains species Z-score values and gives an indication of species performance in relation to each individually defined criterion. Aggregate weighted scores were determined by the formula:
Aggregate weighted score= $W_1X_1 + W_2X_2 ... W_nX_n$. where W = relative weight and X = Z-score value

4.0 MULTICRITERIA MATRIX RAW DATA

4.1 TRANSLOCATION INDEX

Cadmium

Article	Plants	Translocation index (TI) %	Reference number in reference list
Kacprzak et al., 2014	Miscanthus	18	1
	Willow	2	1
	Switch grass	23	1
Afzal et al., 2017	Switch grass	30	156
Liu et al., 2016	Switch grass	9	171
Arora et al., 2016	Switchgrass	17.8	161
Arduini et al., 2004	Miscanthus	65	81
De Maria et al., 2013	Sunflower	23	68
Tahsmabian and Sinegani, 2014	Sunflower	92	180
Kotschau et al., 2014	Sunflower	263	170
de Andrade et al., 2008	Sunflower	23	3
Memoli et al., 2017	Sunflower	62	173
Niu et al., 2007	Sunflower	40	174
Shi and Cai, 2009	Sunflower	28.1	177
	Soybean	5.9	177
	Brassica	29.7	177
Karak et al., 2013	Brassica	37	168
Zhou et al., 2013	Soybean	70	9
	Soybean	93	9
Satpathy and Reddy, 2013	Brassica	124	14
Ali et al., 2017	Brassica	100	158
Bauddh and Singh, 2012	Brassica	62.96	163
Cudic et al., 2016	Poplar	266.3	50
Redovniković et al., 2017	Poplar	111	175
Zacchini et al., 2009	Poplar	10	5
	Willow	23	5
Bonanno and Cirelli, 2017	Typha	12	12

Chromium

Article	Plants	TI %	
Arduini et al., 2006	Miscanthus	13	80
Kacprzak et al., 2014	Miscanthus	165	1
	Salix	17	1
	Switch grass	37	1
Tőzsér et al., 2018	salix	6.3	181
Kotschau et al., 2014	Sunflower	1	170
January et al., 2008	Sunflower	6	7
Memoli et al., 2017	Sunflower	14	173
Han et al., 2004	Brassica	55	55
Singh et al., 2017	Brassica	74	72
Hsiao et al., 2007	Brassica	80	167
Karak et al., 2013	Brassica	64	168
Mei et al., 2002	Soybean	43.5	59
Cudic et al., 2016	Poplar	19.3	50
Bonano and Cirelli, 2017	Typha	20	12

Copper

Article	Plants	TI %	
Kacprzak et al., 2014	Miscanthus	61	1
	Salix	20	1
	Switch grass	52	1
Korzeniowska & Stanislawska-Glubiak, 2015	Miscanthus	14.3	45
Tőzsér et al., 2018	salix	36.3	181
Forte and Mutiti, 2017	Sunflower	76	166
Andreazza et al., 2015	Sunflower	98	159
Kotschau et al., 2014	Sunflower	15.6	170
Memoli et al., 2017	Sunflower	39	173
Rahman et al., 2013	Sunflower	92.5	2
Hsiao et al., 2007	Brassica	93	167
Ali et al., 2017	Brassica	88.9	158
Karak et al., 2013	Brassica	50	168
Blanco et al., 2017	Soybean	147.4	57
Cudic et al., 2016	Poplar	71.9	50
Mendonca and Figueiredo, 2016	Typha	11	4
Bonano and Cirelli, 2017	Typha	30.5	12

Nickel

Article	Plants	TI	
Kacprzak et al., 2014	Miscanthus	92	1
	Salix	9	1
	Switch grass	12	1
Korzeniowska & Stanislawska-Glubiak, 2015	Miscanthus	18.3	45
Tőzsér et al., 2018	salix	62.6	181
Kotschau et al., 2014	Sunflower	60.2	170
January et al., 2008	Sunflower	106	7
Memoli et al., 2017	Sunflower	41	173
Panwar et al., 2002	Brassica	59.2	56
Hsiao et al., 2007	Brassica	50	167
Karak et al., 2013	Brassica	37	168
Salasinska et al., 2016	Soybean	24	24
Cudic et al., 2016	Poplar	38.1	50
Mendonca and Figueiredo, 2016	Typha	27	4
Bonano and Cirelli, 2017	Typha	28	12

Lead

Article	Plants	TI	
Kacprzak et al., 2014	Miscanthus	28	1
	Salix	5	1
	Switch grass	34	1
Toszer et al., 2018	salix	18.6	181
Celebi et al., 2017	Switch grass	4	164
	Sunflower	8.4	164
Arora et al, 2016	switchgrass	16.7	161
Forte and Mutiti, 2017	Sunflower	60	166
Kotschau et al., 2014	Sunflower	1.3	170

Tahmasbian and Sinegani, 2016	Sunflower	30	180
Adedosun et al., 2010	Sunflower	178	13
Memoli et al., 2017	Sunflower	10	173
Rahman et al., 2013	Sunflower	91.8	2
	Brassica	93.1	2
Niu et al., 2007	Sunflower	64	174
	Brassica	51	174
Ali et al., 2017	Brassica	127	158
Karak et al., 2013	Brassica	31	168
Zhou et al., 2013	Soybean	48	9
Cudic et al., 2016	Poplar	49.5	50
Redovnikovic et al., 2017	Poplar	7	175
Mendonca and Figueiredo, 2016	Typha	13	4
Bonano and Cirelli, 2017	Typha	5	12

Zinc

Article	Plants	TI	
Kacprzak et al., 2014	Miscanthus	64	1
	Salix	25	1
	Switch grass	28	1
Toszer et al., 2018	Salix	283	181
Bang et al., 2015	Miscanthus	42.9	162
Korzeniowska & Stanislawska-Glubiak, 2015	Miscanthus	42.3	45
Adedosun et al., 2010	Sunflower	128	13
Kotschau et al., 2014	Sunflower	78.3	170
Satpathy and Reddy, 2013	Brassica	72.2	14
Ali et al., 2017	Brassica	83.3	158
Karak et al., 2013	Brassica	51	168
Zhou et al., 2013	Soybean	119	9
Cudic et al., 2016	Poplar	194.3	50
Romeo et al., 2014	Poplar	49	176
Mendonca and Figueiredo, 2016	Typha	35	4
Bonano and Cirelli, 2017	Typha	30.5	12

2.2 METAL TOLERANCE INDEX

Species	Metals Mg/Kg					
	Cd 32	Cr	Cu 70	Ni 38	Pb 120	Zn 160
Sunflower	89.1 (68)	43.71 (70)	85.71 (69)	40.43 (71)	52.87 (47)	38.41 (67)
	32 (82)					
Brassica	87.4 (8)	32.78 (72)	16.67 (73)	46.4 (6)	33.8 (6)	27.78 (73)
	72.5 (79)					
	46 (82)					
Soybean	64.2 (10)	55 (42)		65.1 (10)		
	44 (82)					
Miscanthus	58.53 (74)	64.1 (75)	53.5 (45)	35 (45)		31 (45)
		46.58 (80)	58.2 (81)			
Poplar	45 (5)		18 (76)		37 (76)	95 (49)

	63 (78)				72.6 (78)	
	54 (83)					
Salix	73 (5)		75.6 (48)		67.6 (43)	115 (49)
	99 (83)					
Switch grass	48.7 (46)	91 (84)				134.5 (44)
	68.2 (84)					106.5 (84)
Typha			78.4 (77)	76.73 (77)		

*Numbers in brackets corresponds with numbered reference in reference list

4.3 CALORIFIC VALUE

Species	Calorific value (MJ per kg)			
Sunflower	18.75 (36)	18.00(97)	18.52 (98)	19.98 (99)
Brassica	18.50 (29)	21.55 (98)	17.61 (111)	17.57 (156)
Soybean	17.59 (30)	16.91 (112)		
Miscanthus	18.64 (20)	19.03(104)	19.58 (105)	18.10 (116)
Poplar	22.20 (32)	19.38 (35)	20.75 (117)	19.50 (118)
Salix	20.07 (33)	19.10 (107)	20.16 (105)	19.75 (104)
Switch grass	18.06 (34)	17.30 (113)	16.17 (114)	18.06 (115)
Typha	19.34 (35)	17.81 (35)		

*Numbers in brackets corresponds with numbered reference in reference list

4.4 BIOMASS YIELD

Species	Dry matter yield (Tons per hectare/year)						
Sunflower	16.025 (37)	13-18.07 (127)	15.95-19.52 (128)	16.3 (142)			
Brassica	9.0 (151)	4.38 (154)					
Soybean	14.13 (38)	8 (155)					
Miscanthus	16.2 (139)	7-10 (119)	7-15 (124)	5-10 (125)	15-24 (123)	4-20 (123)	9-19 (123)
Poplar	8.9 (31)	1.21-9.48 (126)	2.6-5.0 (129)	11.35 (130)	13.34 (131)	17.97 (132)	6.06 (133)
Salix	9.3 (31)	11.6 (120)	1.4-5.8 (129)	8.71-13.01 (134)	7.1-10.1 (135)	1.3-16.3 (136)	13.8 (137)
Switch grass	2.83 – 14.16 (40) 8.5	8.7-12.85 (121)	18.29 (122)	8.96-27.23 (138)	10.2 (139)	4.5-11.4 (140)	8 (141)
Typha	9.2 (39)	16.1 (153)					

*Numbers in brackets corresponds with numbered reference in reference list.

4.5 BIOCHEMICAL COMPOSITION

Species	Biochemical composition (%)			
	Cellulose	Hemicellulose	Lignin	Ash
Sunflower	37.3 (24)	35 (24)	29 (24)	NA
	48.40 (97)	34.60	17	
	26.70 (103)	18.40	27.00	
Brassica	48.3 (151)	29.56	24.56	6.7
	32 (17)	23 (17)	7.6 (17)	1.2 (17)
Soybean	44-83 (15)	18-29 (16)	5-11 (15)	2-5 (15)
	38.00 (110)	16.00	16.00	
	48.00 (111)	17.00	2.00	
Miscanthus	52.13 (21)	25.76 (21)	12.58 (21)	2.74 (21)
	44.70 (106)	29.60	21.00	
	57.90 (107)	16.10	8.00	
Poplar	42.2 (20)	16.60 (20)	25.6 (20)	NA
	49.00 (106)	17.00	18.00	
	48.00 (108)	30.00	22.00	
	47.40 (109)	22.90	31.90	
Salix	48.02 (19)	13.39 (19)	12.38 (19)	1.37 (19)
	82.50(106)	42.10	24.95	
	38.50 (107)	17.60	26.30	
Switch grass	45 (18)	31.4 (18)	12 (18)	NA
	36.80 (100)	32.60	6.30	
	39.60 (101)	38.30	5.90	
	32.00 (102)	32.00	7.00	
Typha	51.03 (22)	31.5 (22)	17.5 (22)	NA
	63 (152)	8.7	9.6	2
	28.7 (153)	23.4	10.1	

*Numbers in brackets corresponds with numbered reference in reference list.

4.6 DROUGHT TOLERANCE INDEX

Species	Moisture treatment							
	Osmotic potential MPa 1	Drought tolerance index 1	OP 2	DTI 2	OP 3	DTI 3	OP 4	DTI 4
Sunflower	-1.62	48.21 (51)	-1.0	72 (143)	-0.8	78 (143)	-1.2	52.5(144)
Brassica	-0.60	77 (52)	-1.17	54.25 (150)				
Soybean	-1.35	33.13 (64)	-0.6	67 (145)	-2.5	55 (146)	-0.41	94 (147)
Miscanthus	-4.6	38-48 (53)						
Poplar	-3.2	55.5 (66)	-2.0	50-58 (149)				
Salix	-1.5	45.59 (65)						
Switch grass	-4.6	18 (54)						
Typha	-1.5	8.40 (63)	-1.0	31.13 (148)				

*Numbers in brackets corresponds with numbered reference in reference list.

4.7. CROP GROWTH RATE

Species	CGR ($gm^{-2}d^{-1}$)	References	Reference number in reference list
H. anuus	9.40 8.61 9.32	Munir et al., 2007 Panneerselvam & Arthanari, 2011 Tribouillois et al., 2015	182 87 26
Brassica	7.30 3.10 3.88	Addo-Quaye et al., 2011 Panda et al., 2004 Tribouillois et al., 2015	90 85 26
Glycine max	3.59 11.80 9.98 8.71	Kumar et al., 2018 Addo-Quaye et al., 2011 Buttery, 1969 Rahman et al, 2011	86 90 89 91
Miscanthus	24.24 23.76	o Di Nasso et al., 2011 El Bassam, 2010	92 93
Populus	0.11	Lamers et al., 2006	96
Salix	0.06	Lamers et al., 2006	96
Panicum virgatum	9.51 8.03	o Di Nasso et al., 2011 El Bassam, 2010	92 93
Typha	6.97 6.69	Kvet, 1971 Dykyjova, 1971	94 95

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