Fakulta zemědělská a technologická
Faculty of Agriculture and Technology
Jihočeská univerzita v Českých Budějovicích
University of South Bohemia in České Budějovice

UNIVERSITY OF SOUTH BOHEMIA IN ČESKÉ BUDĚJOVICE
FACULTY OF AGRICULTURE AND TECHNOLOGY

Department of Agroecosystems

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Title:

Modification of biochar through chemical oxidation to explore the changes in surface characteristics

Author:

Mohammad Ghorbani

Supervisor:

doc. Ing. Petr Konvalina, Ph.D.

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Declaration

I declare that I am the author of this graduation thesis and that I used only sources and literature displayed in the list of references in its preparation.

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Abstrakt

Aplikace biocharu má mnoho výhod v zemědělství a v environmentálních aplikacích. Mnohé povrchové vlastnosti biocharu, jako jsou funkční skupiny obsahující kyslík (FSK) a porézní struktura, mohou být velmi důležité pro adsorpci kationtů v půdě. Modifikace biocharu chemickou oxidací může být považována za způsob, jak zvýšit sorpční vlastnosti biocharu. V první fázi studie byl proveden komplexní přehled dostupné vědecké literatury o biocharu pomocí metaanalýzy dat za účelem volby nejúčinnější modifikační techniky. Následně byla provedena srovnávací fyzikálně-chemická analýza původního a modifikovaného biocharu s peroxidem vodíku (H_2O_2) za použití různých odpadních materiálů. Biouhly byly pyrolyzovány při teplotách 350, 450 a 550 °C a byly získány v různé kvalitě z pšeničné slámy (BPS), žitné slámy (BZS), dřevního odpadu (BDO), třešňových pecek (BDP), čistírenských kalů (BCK) a kravského hnoje (BKH). Praktické využití všech vyrobených biouhlů bylo také testováno z hlediska environmentálních přínosů. Výsledky ukázaly, že pyrolýzní teplota 550 °C u BPS a BZS vedla k tvorbě nově uspořádaných svazků a pravidelných pórů rozptýlených v jejich stěnách. Rentgenová fotoelektronová spektroskopie biouhlů na bázi dřeva ukázala významný nárůst povrchových FSK u O-BDO_{350}, O-BDO_{450}, O-BDO_{550}, O-BTP_{350}, O-BTP_{450} a O-BTP_{550} se zvýšenými hodnotami o 6,5 %, 27,9 %, 42,3 %, 3,9 %, 31,2 % a 52,4 % ve srovnání s jejich biouhly vyrobenými původními metodami. Rovněž účinnost odstranění Cd u O-BTP_{550} (65 %) a O-BDO_{550} (69 %) dosáhla vynikajících výsledků mezi všemi typy biouhlů. Na základě termogravimetrické analýzy byly nejnižší a nejvyšší průměrné ztráty hmotnosti spojeny s BZS (22,5 %) a O-BKH (39,7 %). S ohledem na degradovatelnost surovin a pyrolýzní teplotu tato práce představuje nový přístup k maximalizaci přínosů H_2O_2-modifikovaného biocharu. To nám umožní vytvářet různé biouhly šetrným a ekonomicky méně nákladným způsobem na rozdíl od drahých aktivačních oxidantů. Navíc tento komplexní rozsah je cenný pro pochopení mnohostranné povahy vlastností biocharu, jako je kationtová výměnná kapacita (KVK) a specifický povrch (SP) s určitými modifikacemi, které jsou vysoce relevantní pro aplikaci biocharu do půdy a snížení rizik její kontaminace.

Klíčová slova: biocharu; úpravy; oxidace; výhody absorpce; zlepšení půdy

Abstract

Applying biochar has many advantages in agriculture and environmental purposes. Many surface properties of biochar such as oxygen functional groups (OFGs), and porous structure may be of great importance to address the soil adsorption of cations. Biochar modification using chemical oxidation is considered a promising way to enhance the beneficial sorption characteristics of biochar. In the first stage of the investigation, a thorough evaluation of the literature on the existence of biochar was carried out using a meta-analysis approach to determine the most effective modification technique. Then, a comparative physio-chemical analysis of pristine and modified biochar with hydrogen peroxide (H_2O_2) was conducted using different feedstocks. Biochars were pyrolyzed at temperatures of 350, 450, and 550 °C and were derived from wheat straw, rye straw, wood residues, cherry stone, sewage sludge, and cattle manure, marked as BWS, BRS, BWR, BCS, BSS, and BCM. Also, the practical usage of all produced biochars was tested in terms of environmental benefits. The results showed that the pyrolysis temperature of 550°C in BWS and BRS led to newly arranged vessel formation and regular pores scattered in their walls. X-ray photoelectron spectroscopy of wood-based biochars showed a notable increase in surface OFGs for O-BWR_{350}, O-BWR_{450}, O-BWR_{550}, O-BCS_{350}, O-BCS_{450}, and O-BCS_{550} with increased values by 6.5%, 27.9%, 42.3%, 3.9%, 31.2%, and 52.4% compared to their correspondent pristine biochars. Also, Cd removal efficiency in O-BCS_{550} (65%) and O-BWR_{550} (69%) appeared with outstanding results among all biochar types. Based on thermo-gravimetric analysis, the lowest and highest mass losses on average were related to BRS (22.5%), and O-BCM (39.7%). The study proposes a novel approach to optimize the advantages of H_2O_2-modified biochar by taking into consideration feedstock degradability and pyrolysis temperature. This will enable us to create a variety of engineered biochars cleanly and economically as opposed to costly activation oxidants. Furthermore, this comprehensive scope is valuable for understanding the multifaceted nature of biochar properties such as cation exchange capacity (CEC) and specific surface area (SSA) with certain modifications, which are highly relevant for biochar application in soil amendment and pollution control.

Keywords: Biochar; modification; oxidation; absorption benefits; soil amendment

Content

Chapter 1: Background of Study

1.1. Introduction

Suitable soil performs as an essential component in habitats that are crucial to natural ecosystems, in addition to being a primary processor of human food production. The capacity of the soil to supply moisture, nutrients, aeration, an ideal habitat for microorganisms, and an optimal environment for the growth of plant roots is largely dependent on its structure, which is also the most important aspect (George et al., 2021; Lucas et al., 2019; Yavitt et al., 2021). Several concepts pertain to soil security, fertility, and quality (Bünemann et al., 2018). As an example, the "One Health" idea connects environmental, animal, and health for humans (Keith et al., 2016). It should be noted that Lehmann et al. (Lehmann et al., 2020) distinguished between the definitions of soil quality and soil health. Soil quality is mainly related to ecosystem services concerning people. A lot of authors have already investigated ecosystem services, and this issue is relatively well-described (Krasilnikov et al., 2022; Salomon and Cavagnaro, 2022). Nevertheless, soil health also addresses broader sustainability objectives, such as the health of the planet, in addition to human health (Lehmann et al., 2020). Numerous ecosystem services, such as preserving biodiversity as well as plant and animal productivity, enhancing or maintaining the quality of the water and air, and advancing human health, are dependent on healthy soils (Nannipieri et al., 2003). It is important to remember that even minor changes to the physical, chemical, and biological characteristics of soil can have a direct effect on groundwater pollution, greenhouse gas emissions, heavy metal pollution, and the loss of plant-growth nutrients—all of which pose a threat to the sustainability of the environment and the health of the biosphere (Goswami et al., 2016; Kiani et al., 2021; Pikuła and Stępień, 2021). In the recent decade, scientists have viewed biochar as a modifier and guarantee of soil sustainability due to its adsorption properties (Kamali et al., 2022).

Biochar, as a by-product of the pyrolysis process, has received special attention due to its inherent physical and chemical properties, including the specific surface area and a variety of functional groups in its structure, which make it able to effectively increase soil fertility (Khadem et al., 2021), conserve water resources (Ghorbani et al., 2022), sequester carbon (Gupta et al., 2020), immobilize heavy metals (Chen et al., 2018), increase plant productivity (Ghorbani et al., 2023b) and reduce greenhouse gas emissions from the soil (Yin et al., 2021). Biochar is an efficient and environmentally friendly adsorbent for contaminants since it is a cost-effective, sustainable material with a significant potential for adsorption (Bhavya et al., 2021; Saravanan et al., 2023; Yang et al., 2020). Despite the lengthy innovation process that biochar has gone through over the past 20 years, there is still potential to improve biochar's efficacy in environmental challenges and agriculture. Modification of biochar is an approach to boost biochar benefits in terms of fundamental alterations in biochar structure to make it more effective than pristine biochar. Besides a variety of available feedstock for biochar production as well as pyrolysis conditions play a crucial role in reaching the most efficient biochar Therefore, the main aim of this study was to provide a comprehensive overview of the effects of different biochar modification techniques and pyrolysis conditions on its physicochemical properties and capabilities to overcome agricultural and environmental issues. This study fills a critical gap in the literature by systematically comparing the efficiency of various biochar, which is essential for optimizing biochar for specific applications in agriculture and environmental management. This comprehensive scope is valuable for understanding the multifaceted nature of biochar properties such as cation exchange capacity (CEC) and specific surface area (SSA) with certain modifications, which are highly relevant for the application of biochar in improving soil nutrient productivity, remediation of polluted soil and mitigation of greenhouse gases emissions.

1.2. Literature review

1.2.1. The role of biochar in sustainable crop production

The improvement of plant productivity is unavoidable due to its porous structure and ability to retain water (Asadi et al., 2021), nutrients (Ghorbani et al., 2019), and limit the absorption of pollutants such as heavy metals by plant roots (Amirahmadi et al., 2020). For example, cereals are among the most important crops that contribute significantly to the global supply of essential minerals, carbohydrates, and proteins in the world (Laskowski et al., 2019). According to reports, inadequate management of irrigation, a lack of organic matter in the soil, and a lack of expert chemical fertilization would significantly reduce the production of crop harvests, both quantitatively and qualitatively (Sharma et al., 2020). However, an ideal agricultural operations plan must include the best possible and balanced nutrient management. The plant needs energy from sunshine, water, and carbon dioxide together with nutrients including nitrogen (N), phosphorus (P), and potassium (K) to generate the product.

According to published research, biochar's structural characteristics are resistance to degradation with time which makes it a sustainable material for crop-production benefits (Deng et al., 2020; Ghorbani et al., 2021; He et al., 2019; Li et al., 2017; Mia et al., 2017). In other words, biochar is seen to be among the most effective approaches to achieving environmentally friendly, sustainable agriculture with net zero emissions. It is worth noting that, recent years have led to a significant increase in biochar application in farming systems to enhance photosynthesis and plant development (Ghorbani et al., 2021; Liu et al., 2013). Several factors increase plant photosynthesis following biochar addition, such as the higher availability of water and nutrients (especially nitrogen), the higher cation exchange capacity (CEC) and porosity of the soil, more active microorganisms, as well as the immobilization of toxic metals (Liu et al., 2019; Tomczyk et al., 2020). On the other hand, two main types of photosynthetic structures (C3 and C4 plants) can have different responses to biochar. C4 plants have a more advanced mechanism for photosynthesis and stabilization of atmospheric carbon dioxide than C3 plants due to their physical structure (Li et al., 2019). C3 plants, such as rice or wheat, fix CO_2 directly from the atmosphere and in mesophyll cells, while in C4 plants, such as maize or sugarcane, that process is conducted in specialized mesophyll and bundle sheath cells to participate in photosynthesis that is anatomically and biochemically distinct (He et al., 2020). Typically, C4 plants have a 50% higher efficiency in photosynthesis rate (Pn) than C3 plants (Li et al., 2019). Regarding the role of soil metal toxicity in reducing plant photosynthesis efficiency, it should be noted that biochar addition to soil is also considered for preventing plants from heavy metal toxicity (Amirahmadi et al., 2020; Gorovtsov et al., 2020). The concentration and toxicity of heavy metals have been widely considered in recent years due to the specific environmental problems they cause. The presence of heavy metals in soils, even in very low amounts, disrupts plant functions (Amirahmadi et al., 2020). Cadmium (Cd) is one of the heavy metals that constitutes negative effects on ecosystems and food chain health (Oni et al., 2019). Cd enters the soil through employing insecticides, irrigation with wastewater, and fertilization, as well as via metal retrieval industries. It has been widely shown that the presence of Cd in the soil causes a reduction in plant growth, such as a reduction in root length and leaf number (Haider et al., 2021), and disturbances in carbohydrate metabolism (Gorovtsov et al., 2020) and the photosynthetic system (Liu et al., 2019). Prevention of chlorophyll synthesis is the main result of Cd bioaccumulation that is exhibited with biomass deficit and Pn reduction (Ahmad et al., 2019). Cd stress furthermore alters stomatal movements, ion homeostasis, and respiration in plants, and also prohibits the activities of enzymes (Xiaoxia Zhang et al., 2020). Typically, the existing methods for reducing negative effects on plant growth are, however, costly and applicable to remediate small areas (Amirahmadi et al., 2020). For example, enhanced phytoremediation of Pb-and Cd-contaminated agricultural soil with crops seemed not to be suitable in a reasonable time (Neugschwandtner et al., 2012). Furthermore, there is the risk of destruction of soil structure, disruption of soil biological activities, and environmental pollution (Haider et al., 2021). Therefore, it is essential to provide a reliable and cheap method that minimizes contamination at low costs and is relatively fast without adverse effects on environmental health (Ghorbani et al., 2019; Xiaoxia Zhang et al., 2020). It has been widely shown that biochar can trap heavy metals in the soil and thus reduce their toxicity by relying on its unique characteristics such as high porosity and surface area (Ahmad et al., 2019; Amirahmadi et al., 2020). However, the use of biochar in soil is influenced by soil characteristics and fertilizer management (Gao et al., 2021). It has been suggested that the co-application of biochar and organic fertilizers could mainly boost maize, peanut, and cowpea yields in a setting with depleted soil (M. Liu et al., 2022). To increase maize production, the use of biochar on maize needs to be paired with the required amount of N, P, and K fertilizers as well as plant nutrition systems (Ghorbani et al., 2022; Peng et al., 2021).

1.2.2. The relationship between biochar and nutrient status in plant and soil

Thus far, research has been done on the usefulness of biochar in a variety of agricultural and environmental domains, including boosting soil and plant production (Raza et al., 2023), disinfecting up soil and water bodies (Ai et al., 2023), minimizing greenhouse gas emissions (Zhang et al., 2019), and capturing organic and mineral contaminants (X. Li et al., 2023; Qiu et al., 2021). The porous nature of biochar, significant specific surface area, high absorption capacity, and high resistance to decomposition are the key characteristics of biochar that have turned it into a multifunctional material (Hai et al., 2023; Liao et al., 2021). It has been shown that biochar application improves soil fertility and properties and helps stabilize heavy metals, which lowers the amount of heavy metals absorbed by plants through ion exchange, physical adsorption, and electrostatic attraction (Ibrahim et al., 2023; Shaheen et al., 2023; J. Zhang et al., 2020). Numerous research have looked into the prospect of using biochar to support plants that are under salt stress (Ali et al., 2017; Kim et al., 2016).

It has been shown that, under drought stress, biochar strengthens the physicochemical characteristics of the soil and increases its ability to retain water (Ghorbani et al., 2022; Lalay et al., 2022). In addition to providing nutrients, applying biochar to soil under cropping systems provides the advantage of changing soil properties including crop productivity, cation exchange capacity, and water-holding ability (Ye et al., 2020). According to reports, applying biochar may boost crop yield since it raises pH, stores more carbon in the soil, and helps crops retain water and nutrients (Asadi et al., 2021; Wei et al., 2020). Carbon sequestration, soil productivity, and the immobilization of both organic and inorganic contaminants can all be enhanced by using biochar (Amirahmadi et al., 2020; Luo et al., 2023). Also, it has been demonstrated that biochar both physically protects soil microorganisms and concurrently boosts microbial resilience to potentially harmful element stress, both of which are helpful to the health of soil and plant root (Yang et al., 2023).

Furthermore, it has been reported that the application of biochar significantly improved the properties of the stem cell walls, with increases of 52% in stem breaking force which is thought to be an important factor in the increased biomass yield and lodging resistance (Miao et al., 2023). According to another study, utilizing biochar made from rice hulls can significantly increase the levels of lignin and silicon in stalks, increasing the stalks' resistance to lodging (Gong et al., 2024). However, depending on the pyrolysis conditions and feedstock types, biochar's efficacy in treating factors associated with lodging tolerance differs (Ghorbani et al., 2024; L. Li et al., 2023). It has been shown that the soil treated with biochar has a higher capacity for cation exchange owing to its high specific surface (Hailegnaw et al., 2019). Due to its porous nature, biochar facilitates the growth and habitation of a broad range of microorganisms that break down organic molecules, hence fostering the availability of nutrients for plant roots. Using more biochar increases the potential for microorganism growth and development resulting in plant productivity. It has been reported that applying rice husk biochar at a rate of 30 t ha^{-1} can dramatically enhance rice biomass output by up to 29% (Miao et al., 2023). Additionally, previous investigations have shown that biochar improved rice's absorption of the key nutrients—nitrogen, phosphate, potassium, and iron—which raised biomass output (Chew et al., 2020; Li et al., 2015). Rice biomass was shown to have significantly risen because of the biochar-rhizosphere interaction, which was claimed to have raised the membrane potential difference between the soil and the root. This, in turn, decreased the free energy needed for root nutrient accumulation (Chew et al., 2022). It should be mentioned that the fact that husk biochar gives plants a lot of silicon accounts for its effectiveness in plant resistance indices (Asadi et al., 2021; Ghorbani and Amirahmadi, 2018). Consequently, the plant stems' cell wall thickness has expanded dramatically because of the transfer and deposit of silicon from the rich silicon-treated soil treated with husk biochar (Zhang et al., 2015). Also, by binding cellulose microfibrils to lignin and bonding them together, hemicellulose, a class of heterogeneous polysaccharides, contributes significantly to the reinforcement of cell walls (Landi and Esposito, 2017; Qaseem et al., 2021). According to reports, lignin and silica content in rice plants treated with biochar from rice husks increased by 13% and 58%, respectively (Miao et al., 2023).

1.2.3. Biochar production and its chemistry

While the utilization of biochar has the potential to tackle a wide range of environmental and agricultural issues, it indicates some obstacles have limited the full capability of biochar. It has been demonstrated that the efficiency of biochar is directly impacted by the variety of feedstocks used, each of which has unique properties of its own. (Wallace et al., 2019; Yang et al., 2019). The type of feedstock and its C/N ratio are important factors as they directly affect the forming of the porous structure and absorbent characteristics of the biochar during the pyrolysis process (Farrar et al., 2019; Tomczyk et al., 2020). There are contemporary reports on the effects of biochar derived from different types of feedstocks on photosynthesis and plant growth (Farrar et al., 2019; Nguyen et al., 2017). For example, wood residues, bamboo, and plant stems are relatively hard feedstocks with a C/N ratio >50. Consequently, their degradability in the pyrolysis process is lower than that of feedstocks such as rice hull, rice straw, or wheat straw (Asadi et al., 2021). Thereby, the potential effectiveness of biochar derived from feedstocks with a higher C/N ratio will decrease in the root zone as the number of negative charges and functional groups on the biochar surface is lower (Giles et al., 2017). In general, wood and crop-based feedstocks that contain lignin, cellulose, and hemicellulose are better suited for purifying up organic pollution and reducing greenhouse gas emissions, whereas biochar originated from sewage sludge and manure with significant amounts of ash are more effectively appropriate for heavy metal and cationic organic pollutants (Ji et al., 2022). In soils which are unable to retain nutrients and water, having a porous bulk with a well-developed surface area is essential for plant growth (Zi et al., 2023). As a result, adding biochar derived from straw—rather than biochar derived from wood—could be more effective since it supplies nitrogen and other macronutrients that are crucial for plant growth (Asadi et al., 2021).

Furthermore, the range of pyrolysis settings increases the challenges of producing the most effective biochar (Gui et al., 2020; Munera-Echeverri et al., 2018). It has been stated that soil treated with biochar carbonized at a higher pyrolysis temperature than a lower one showed a significant increase in soil aggregation and carbon pool index (Ghorbani et al., 2023c). Therefore, it is inevitable that a wide range of possibilities regarding various types of feedstocks and pyrolysis conditions will arise in the formation of intrinsic biochar characteristics. Meanwhile, disorganized conditions could lead to incompatible and ineffective biochar. Inaccurate biochar processing causes unwanted properties such as low porosity, underdeveloped specific surface area, restricted capacity to absorb contaminants, decreased capacity to hold onto water and nutrients in the soil for plant development, and elevated concentrations of pollutants (Fan et al., 2018; Ghorbani et al., 2023a; Li et al., 2022).

1.2.4. Engineered biochar through modification techniques

Biochar modification is a further approach, besides identifying an appropriate production strategy, that could assist us get much closer to producing the most efficient biochar. Several studies have shown that fundamental changes in the physicochemical structure of biochar, including a decrease in volatility, an increase in micropores, an expansion of the specific surface area, and an increase in several functional groups such as carboxyl and hydroxyl, occur as the pyrolysis temperature rises (Bayoka et al., 2023; Ghorbani et al., 2024; L. Li et al., 2023). As a result, these alterations improve biochar's ability to absorb cations and release cations such ammonium that are essential for plant growth. It is obvious that plant function can be significantly impacted by applying a higher amount of biochar. Previous research demonstrated that biochar improved plants' key nutrient NPK absorption, increasing biomass output (Chew et al., 2020). Currently, several modification techniques are suggested to boost biochar characteristics, including steaming, chemical oxidation, physical activation, and so on (Fan et al., 2018; Foong et al., 2020; Kumar et al., 2020). Of these, chemical modification - mostly including acids, bases, and metal oxides - is the method most used to modify biochar. Some researchers have found that oxidation improves the surface adsorbent characteristics of biochar, such as increasing the cation exchange capacity (CEC) and oxygen-containing functional groups (Li et al., 2017). The addition of oxidized biochar to soils may be more beneficial than adding fresh biochar because the deterioration of biochar properties during oxidation increases the capacity of soils to retain water and nutrients (Mia et al., 2017). It has been reported that oxidation in biochar can effectively promote the breakdown of organic molecules in soil, and then the neutralization of alkaline status (Hadjittofi et al., 2014). Furthermore, it has been found that applying biochar subjected to oxidative agents improves moisture availability (Toková et al., 2020).

According to reports, aging biochar through freeze-thaw and dry-wet procedures resulted in a significant increase in its surface area, pure volume, and oxygen functional groups (OFGs) as compared to unaged biochar (Zhang et al., 2022). Several studies have demonstrated that chemical composition changes enhance the hydrophilicity of biochar surfaces and increase the amount of OFGs and metal cation-absorption capacity (B. Li et al., 2021; X.-J. Liu et al., 2021; Z. Liu et al., 2022). Based on reports, goethite-modified biochar has 63 times more potential than untreated biochar to adsorb arsenic from contaminated water (Zhu et al., 2020). In a study, the interactions of pyrolysis temperature and feedstock in H_2O_2-modified biochar were investigated and it has been reported that H_2O_2 oxidation can considerably assist in the formation of a variety of pores and vessels in modified biochar with a diameter range of 10–30 μm in small ones and 30–100 μm in large ones (Ghorbani et al., 2024). Also, the frequency of tiny pores in agricultural-based feedstocks was higher than in wood-based feedstocks. In another study, wood biochar treated with $KMnO_4$ has the potential to dramatically absorb more cadmium when compared to unmodified biochar due to a substantial alteration in the biochar's specific surface area (Wang et al., 2015). Compared to the pristine biochar, the engineered biochar treated with $ZnCl_2$ showed a larger amount of elemental oxygen (24 weight %). On the other hand, the weight concentration of structural carbon substantially decreased from 82 % in fresh biochar to 27 % in modified biochar (Iwuozor et al., 2023).

1.3. Objectives and Hypotheses

The previous research on H_2O_2 oxidation in biochar has focused on one particular type of biochar, derived from a particular feedstocks. The main aim of this study is to achieve an accurate understanding of the biochar-H_2O_2 oxidation mechanism that could be obtained by comparing the function of H_2O_2 in several biochars with various origins in a single study. This is crucial because different feedstocks have varying degrees of resistance to breakdown and lead to differing intrinsic properties in the final biochar products. Additionally, the engineering approach of producing biochar under various pyrolysis, feedstock, and modification circumstances while implementing a variety of advanced laboratory analyses is quite rare. Therefore, we hypothesized that applying H_2O_2 oxidation and changing the pyrolysis temperature would significantly increase the absorption characteristics of biochars generated from different feedstocks. For this purpose, we compared 36 biochars with various properties, including unmodified and H_2O_2-modified biochars made from six feedstocks that fall into three categories of degradability, i.e., resistant (wood residues and cherry stone), medium (wheat straw and rye straw), and weak (sewage sludge and cattle manure), each produced at three pyrolysis temperatures (350, 450, and 550 °C). Also, to examine our hypothesis, we tested the actual effectivness of the produced biochar from different agricultural and environmental aspects such as heavy metal immobilization, soil aggregation, and soil carbon status. It is anticipated that the production and characterization of these engineered biochars will lead to a better comprehension of the biochar boosting process using the H_2O_2 modification technique, as well as opening up the prospect of their implementation for a variety of applications including soil amendment, plant productivity, environmental pollution adsorption, sustainable biomass conversion engineering, and mitigation of greenhouse gas emission.

Chapter 2: Methodology

2.1.Meta-Analysis approach

2.1.1. Literature survey and eligibility criteria

A meta-analysis method was carried out to obtain a comprehensive understanding of the matter and to determine the most effective biochar and modification strategy for maximizing biochar's potential as well as elevating its intrinsic characteristics. Using the Web of Science and Google Scholar websites, studies that reported on cation exchange capacity (CEC), micropores (MP), specific surface area (SSA), and oxygen-content functional groups (OFGs) in non-oxidized (control) and oxidized (treatment) biochar were selected. Keywords used for the literature search were combinations of terms such as biochar, pyrolysis, feedstock, oxidation, aged biochar, soil, surface area, porosity, functional, groups, and CEC. The following main criteria were applied to select appropriate studies: (i) all studies reported results from a non-oxidized (control) and oxidized (treatment(s)) biochar, (ii) studies without replicated treatments and control as defined had been ignored, and (iii) published in a peer-reviewed journal; (iv) published in English; (v) data available for at least 2 target variables; (vi) all studies were published from 2011 to 2021.

2.1.2. Collection of data

Nearly 600 papers were overlooked and of that, 64 studies satisfied our criteria for inclusion. In this meta-analysis, 1822 observations or 911 pairs of observations (effect sizes) were retrieved from the papers that matched our criteria. These datasets consisted of the CEC, MP, SSA, and OFGs of oxidized (treated) and non-oxidized (control) biochar affected by types of oxidations, time of modification, pyrolysis temperature, and types of feedstocks. The extracted analytical data were standardized to the same metric for each property (CEC in $cmol^{(+)}kg^{-1}$, MP in $cm^3\ g^{-1}$, SSA m^2g^{-1}, and OFGs in %) to allow for comparison among different studies. Ammonium acetate, BET method, and FTIR spectra were the most used methods for measuring CEC, MP, SSA, and OFGs in the selected articles. Different types of oxidation were categorized as acidic (HNO_3, HCI, H_2O_2, …), alkalic (NaOH, KOH, …), metal oxides ($Zn(NO_3)_2$, Fe_2O_3, MnO, …), physical (freeze-thaw, dry-wet, steam) and natural (organic acids, soil minerals, microbial aging). Pre-pyrolysis and post-pyrolysis were considered in determining the time of modification. Pyrolysis temperatures were classified as low (<400°C), medium (400-550°C), and high (>550°C). according to the nature of feedstocks, they were grouped based on decomposability as follows; (i) resistant, referring to feedstocks like tree parts, wood, sawdust, etc.; (ii) intermediate, referring to herbaceous and agricultural biomass such as straws, shells, etc.; (iii) unstable, referring to waste biomass like manure, sewage sludge, solid waste, algal biomass etc (L. Wang et al., 2020).

2.1.3. Meta-data analyses

Meta-analysis determines the extent of a variable's change and its relevance in response to an oxidation. The magnitude of the change is referred to as the effect size. The natural logarithm of the response ratio (RR) (Eq. 1) was used to compute the effect size (Hedges et al., 1999):

$$\ln(RR) = \ln\left(\frac{X_T}{X_C}\right) \tag{1}$$

X_C and X_T are the means of the variable in the control and treatment, respectively. The RR can be thought of as $(e^{\ln(RR)} - 1) \times 100$, which is the percentage change following oxidation (Nave et al., 2010). We recorded the standard deviation (SD) and number of replicates (n) of CEC, MP, SSA, and OFGs for the control and treatment groups to generate confidence intervals (CIs) around effect sizes. If a study provided standard error (SE) or coefficient of variation (CV), the SD was determined using the formulas $SD = SE \times \sqrt{n}$ and $SD = CV \times mean$. For each effect size, the statistical significance was determined using the 95% CIs. If the 95% CIs ($P \leq 0.05$) did not intersect the zero line, the group means were substantially different. In some of the studies examined, CEC, MP, SSA, and OFGs were all reported at the same time, allowing regression tests to be conducted to check whether any interdependencies existed. The data analysis and organizing were conducted using the MetaWin 2.1 software (Rosenberg Software, Arizona State University, Tempe, AZ, USA). Data were extracted from the tables directly or extracted from the figures using GetData Graph Digitizer 2.24 software (Getdata Graph Digitizer, Fedorov S, Krasnoyarsk, Russia). The design of forest plots and regression analysis were carried out with IBM SPSS Statistics v24.

Publication bias was assessed using Funnel plots and Egger tests (Hedges et al., 1999). Rosenberg's fail-safe-numbers (*Nfs*) were calculated to assess the robustness of biochar CEC, MP, SSA, and OFGs (Table 2) to the publication bias (Schmidt et al., 2021). The results were considered robust despite the possibility of publication bias if $Nfs > 5 * n + 10$, where n indicates the number of sizes. The biochar data for any of the parameters did not contain any evidence of publishing bias.

The heterogeneity of overall effect sizes between groups was tested using random-effect models to explore the effect of oxidation on biochar surface characteristics concerning the various affecting factors (types of oxidations, time of modification, pyrolysis temperature, and types of feedstocks). Each factor (e.g., pyrolysis temperature) was divided into different categories (e.g., low, medium, and high temperatures) to identify the significant differences among their effect sizes. Total heterogeneity (QT) was partitioned into within-group (QW) and between-group (QB) variations for each category variable. We determined the significance of the between-group heterogeneity (QB) using a randomization test (Adams et al., 1997) to ascertain whether the mean effect sizes of the categories varied between the levels of the factors. To examine the significance of the remaining within-group heterogeneity (QW), we performed a chi-squared test. The Q statistic follows a chi-square distribution with n-1 degrees of freedom, where n is the total number of paired data between oxidized and non-oxidized treatments for a variable. It is assumed that variables with low P values ($p < 0.05$) and high QB values are better able to predict changes in the total effect size. To analyze the existing correlation between biochar characteristics, linear regression was performed using SPSS. v24 software as follows: a) mean of predicted values and residuals, b) normality of unstandardized residues values ($p > 0.05$) by Shapiro-Wilk test, c) the existence of potential outliers by Cook–Weisberg test, (d) the presence of autocorrelation between regression variables by Durbin-Watson test and e) the significant of the regression model by Fisher–Snedecor test significance.

2.2.Biochar production

To obtain a comprehensive analysis of biochar, six feedstocks were collected from three different categories of raw materials as follows: wheat straw (WS) and rye straw (RS) as crop residues which represent soft raw lignocellulose materials; wood residues (WR) and cherry stone (CS) as wood-based feedstocks which represent hard raw lignocellulose materials; sewage sludge (SS) and cattle manure (CM) as easily decomposable feedstocks. All feedstocks were carbonized using an electric muffle furnace (Nabertherm, Lilienthal, Germany). The pyrolysis process was carried out at temperatures of 350, 450, and 550 °C, with a heating rate of 10 °C min^{-1}, a residence time of 2 h, and under nitrogen flush gas to an oxygen-free interior of the muffle. To remove impurities, all six biochar samples were rinsed two times with deionized water and dried at 105 °C in an oven for 24 h. The dried samples were then ground and sieved to a uniform size fraction of 0.5–1.0 mm. Then, each biochar sample was divided into two portions; 1) the first portion was stored as pristine biochar, and 2) the second one was kept for applying H_2O_2 oxidation to achieve oxidized biochar. In the oxidation process, 10 g of biochar samples were exposed to 50 mL of 30% H_2O_2 solution (purchased from Penta Chemical, Prague, Czechia) in a 100 mL glass beaker and were stirred for 2 h at a constant temperature of 70 °C). Each sample was then filtered through Whatman filter paper No. 42 and rinsed with deionized water to remove any residual H_2O_2 (Tomczyk and Szewczuk-Karpisz, 2022). The samples were then dried in an oven at 105 °C for 24 h. At the end, we had 36 biochars because of six different feedstocks, three pyrolysis temperatures, and two oxidized and non-oxidized conditions.

2.3. Biochar analysis

2.3.1. Basic and ultimate analysis

The pH and EC of biochar were determined using a 1:10 (w/v) ratio suspension of biochar and deionized water (Fidel et al., 2017). In short, 0.1 g cm^{-3} suspension of biochar-deionized water was shaken for 5 h. The biochar suspensions were then measured for both pH and EC using AI212 pH/EC20 meters (APERA instruments, Shanghai, China). The ammonium acetate technique was used to determine cation exchange capacity (CEC) (Munera-Echeverri et al., 2018). Concisely, 1 g of each biochar sample, was shaken for 1 h with 20 mL of deionized water. Then, 0.05 M HCl was gradually added to the sample until it reached pH 7.0 ± 0.3, subsequently, again 1 h shaking was conducted. The sample was then filtered and washed with deionized water three times. These washing steps were conducted to remove readily soluble cations associated with salts, ashes, and weak acid functional groups that may affect CEC value. The samples were then dried at 105 °C for 6 h. To release exchangeable cations from the sample, 0.5 g of dried samples were re-suspended in 20 mL 1 M NH_4OAc. After 1 h shaking, samples were filtered and the filtrates were stored for analysis of base cations by inductively coupled plasma optical emission spectrometry using ICP-OES-5900 (Agilent Santa Clara, USA) and the CEC calculated based on the sum of exchangeable base cations.

For ultimate analysis, an elemental analyzer TruSpec Micro CHNS (Leco, Michigan, USA) was used to detect the elemental composition of biochars including carbon (C), hydrogen (H), nitrogen (N), and sulfur (S). Briefly, 0.05 g oven-dried samples were used to determine the percentage of CHNS elements in biochar structure. Oxygen (O) content was calculated using Eq. (2):

$$\mathrm{O}\ (\%) = 100 - [\text{CHNS content}\ (\%) + \text{Ash content}\ (\%)] \qquad (2)$$

Molar ratios of O/C, H/C, and C/N which represent the bonding arrangement and polarity (Suliman et al., 2016) were obtained by dividing the percentage of each element in the CHNS analyzer by their specific atomic weights.

2.3.2. Proximate analysis

The biochar yield (BY) was calculated using the initial weight of feedstock and the immediate weight of produced biochar as shown in Eq (3). The moisture content (MC) of biochar was obtained by weighing the biochar samples before and after drying in an oven at 105 ºC for 24 h using Eq (4). The ash content (AC) and volatile matter (VM) of biochars were measured using an electric muffle furnace (Nabertherm, Lilienthal, Germany). To obtain the ash content, 1.5 g of oven-dried biochar samples were weighed into a pre-weighed crucible and heated in air at 600 °C for 6 h. After combustion, the residues were weighted, and the ash content was calculated according to Eq (5). For volatile matter determination, 8 mg of oven-dried biochar samples were burned at 950 °C for 30 mins under a nitrogen atmosphere and then the weight of the remaining mass after combustion was used for volatile matter calculation based on Eq (6). Fixed carbon (FC) was calculated by subtracting the percentages of moisture, ash, and volatile matter from the initial biochar weight as shown in Eq (7).

$$\text{Biochar yield (\%)} = [\frac{\text{Feedstock weight (g)} - \text{Biochar weight (g)}}{\text{Biochar weight (g)}}] \times 100 \quad (3)$$

$$\text{Moisture content (\%)} = [\frac{\text{Initial biochar (g)} - \text{Oven dried biochar at 105 ºC (g)}}{\text{Oven dried biochar at 105 ºC (g)}}] \times 100 \quad (4)$$

$$\text{Ash content (\%)} = [\frac{\text{Oven dried biochar at 105 ºC (g)} - \text{Combusted biochar at 600 ºC (g)}}{\text{Combusted biochar at 600 ºC (g)}}] \times 100 \quad (5)$$

$$\text{Volatile matter (\%)} = [\frac{\text{Oven dried biochar at 105 ºC} - \text{Combusted biochar at 950 ºC (g)}}{\text{Combusted biochar at 950 ºC (g)}}] \times 100 \quad (6)$$

$$\text{Fixed carbon (\%)} = 100 - [\text{Moisture content (\%)} + \text{Volatile matter (\%)} + \text{Ash content (\%)}] \quad (7)$$

2.3.3. Physical analysis

To analyze the specific surface area (SSA) and micro-pores (V_{micro}) of biochar samples, the Brunauer-Emmett-Teller (BET) method was conducted with nitrogen adsorption/desorption isotherms obtained at 196 °C using ASAP 2420 apparatus (Micromeritics, Georgia, USA). The biochar bulk density (Bd) and total porosity (V_t) of biochar samples were measured with a mercury porosimetry AutoPore IV 9500 M (Micromeritics, Georgia, USA).

2.3.4. Advanced analysis

A scanning electron microscope with energy dispersive spectroscopy (SEM-EDS) was used for the visualization of biochars and elemental characteristics of the surface using the TM3030 microscope (HITACHI, Tokyo, Japan). Before imaging, a steady layer of platinum coating was applied to the surface of the samples using EM ACE200 vacuum coater (LEICA, Wetzlar, Germany), with the purpose of obtaining high-resolution images of the biochar structures using the SEM.

X-ray photoelectron spectroscopy (XPS) was conducted to analyze the surface atomic composition of the biochars before and after oxidation using an ESCALAB 250Xi (ThermoFisher, Massachusetts, USA) with X-ray radiation of 1253.6 eV as XPS excitation source for acquiring all photoelectron spectra. The C1s bending energy ranges were assigned from 284.5 to 288.5 eV, whereas O1s were between 529 and 533 eV.

The crystal structure of the biochar samples was analyzed by X-ray diffractometer (XRD) using X'Pert Pro (PANalytical, Malvern, UK). The diffractometer was operated at 40 kV and 40 mA using a Cu Kα radiation source. Diffractograms were in the range of 4°-70° (2θ scale) at a step size of 0.02° and a counting time of 1.2 s per step.

To analyze the status of functional groups on the surface of biochar samples the fourier transform infrared spectroscopy (FTIR) was conducted in the wavenumber region of 400-4000 cm^{-1} by using FTIR Spectrum 3 (PerkinElmer, Massachusetts, USA).

Thermo-gravimetric analysis (TGA) was conducted to analyze the thermal stability of biochar samples using TGA4000 (PerkinElmer, Massachusetts, USA). In short, 0.5 biochar samples were placed in a crucible made of alumina and heated at a rate of 10 °C min^{-1} over a range of 20-1000 °C. The purge gases through the TGA were purified N_2.

To determine the high heating value (HHV) of oxidized and non-oxidized biochars, a bomb calorimeter C200 (IKA, Staufen, Germany) was used. Summarily, 0.5 g biochar samples were weighed into the crucible and put into the copper vessel of the calorimeter which contains water. After burning the sample in oxygen-rich condition, the released heat from the combustion into the water container was measured by a thermometer.

2.4.Biochar practical usage

Practical effectiveness of biochar, eighter pristine or modified biochars, were tested in some individual experiments. The experiments were included in a vast range of agricultural and environmental topics. In general, the efficiency of the biochar was assessed in soil properties, greenhouse gas (GHG) emissions, and heavy metal immobilization. Brief information on used methods for the measurement of parameters is presented as follows.

2.4.1. Soil basic characteristics

Soil samples were analyzed by the following methods: soil pH and electrical conductivity (EC) in a 1:1 (w:v) by soil-to-water ratio; soil texture by hydrometer; organic carbon (OC) by wet oxidation (Mingorance et al., 2007); available N (NO_3^- and NH_4^+) were determined using a continuous flow analyzer (SEAL Analytical, Germany) with 1 M KCL extracts (Fu et al., 2019); available P was determined using sodium bicarbonate method (Horta and Torrent, 2007). Soil K was determined using the flame photometer method (Lu et al., 2017); exchangeable basic cations were analyzed using a 5:50 ratio of soil:ammonium acetate (NH_4OAc)-buffered solution at pH 7, in which the basic cations adsorbed in soil were replaced by NH_4^+ ions (Tournassat et al., 2004) and measured by spectroscope (ICP-OES, PerkinElmer); exchangeable acid cations (Al^{3+} and H^+) was determined by the KCl extraction method (Kostin et al., 2021). Also, the effective cation exchange capacity (ECEC) was determined by summation of the respective exchangeable bases and exchangeable acidities. The soil bulk density (BD) was measured by the clod method, and then the soil porosity was calculated using BD values (Xu et al., 2016). Spectrophotometry (PerkinElmer Optima 7300V) was used to estimate the quantity of soluble base cations (Ca^{2+} and Mg^{2+}), and the flame photometer was used to calculate Na+ (M410 Sherwood). The sodium absorption ratio (SAR) was then computed using the following equation (Eq. 8):

$$\text{SAR} = \frac{Na^{+}}{\sqrt{\frac{Ca^{2+} + Mg^{2+}}{2}}} \times 100 \tag{8}$$

2.4.2. Carbon indices

A Primacs SLC Analyzer (SKALAR, Netherlands) was used for determining soil carbon status including total carbon (TC), total organic carbon (TOC), and total inorganic carbon (TIC). The carbon pool index was calculated as follows (Blair et al., 1995) (Eq. 9):

$$\text{Carbon pool index (CPI)} = \frac{\text{SOC}_\text{b}}{\text{SOC}_\text{c}} \tag{9}$$

where, SOC_b and SOC_c are the soil organic carbon content of the biochar treatments and the control, respectively. The potential for carbon sequestration following the application of biochar was then explained using the CPI, which shows the impact of biochars on the storage of total soil carbon. Greater OC formation or loss is indicated by a higher CPI (CPI > 1) or a lower CPI (CPI < 1).

2.4.3. Soil moisture status

Using porous plate funnels and pressure plate equipment, the soil water content curves were calculated (Robertson et al., 2022). The imposed tensions were 0, −10, −33, −100, −300, −500, and −1500 kPa which are equals to 0, 2, 2.5, 3, 3.5, 3.7, and 4.2 pF (log matric potential). The field capacity (FC) and the permanent wilting point (PWP) were determined to be −33 and −1500 kPa, respectively. Three replications were performed. The difference between FC and PWP was used to compute the available water content (AWC). The soil water retention curve was used to determine the volume of macro-pores (>10 m), meso-pores (0.2-10 m), and micro-pores (<0.2 m), which correspond to <2.5 pF, 2.5-4.2 pF, and >4.2 pF (Sakai, 1994). The Ks were determined in a laboratory setting using the constant-head method at 0.1 kPa pressure by applying a steady hydraulic head to the top of water-saturated cores (Klute, 2015).

2.4.4. Soil aggregation

The aggregate size distribution was investigated using the wet sieving procedure. For this purpose, 10 g of soil was dried in an oven at 105 °C for 12 h, then wetted with tap water for around 24 hours. Once the soil had rested in a water container, it was sieved for 10 minutes at a rate of 35 cycles per minute using a set of sieves with holes that were 2, 1, 0.5, 0.25, and 0.053 mm in size. The remnant particles in each sieve were wet shaken, collected gently, and dried at 105 °C for 24h. To calculate the aggregate size distribution, the weight ratio of materials from each sieve to the total weight of materials was determined. Also, the mean weight diameter (MWD) of the soil aggregates was obtained using the following equation (Kemper and Chepil, 2015) (Eq. 10):

$$\text{Mean weight diameter } (MWD) = \Sigma_{i=1}^{n} \bar{X_i}\, W_i \qquad (10)$$

where $\bar{X}$ is the average diameter of the aggregates on each sieve, Wi is the weight ratio of aggregates per sieve to the total weight of the soil, and n is the number of used sieves.

To evaluate water-stable aggregates (WSA), 4 g of 1-2 mm air-dried aggregates were placed on a 0.26 mm sieve, and then shaken in a water container for 3 minutes and with a speed of 35 times min^{-1} at a distance of 1.5 cm (Kemper and Chepil, 2015). After drying samples in the oven at 105 °C for 24 h, the water-stable aggregates (WSA) were calculated using the following equation (Eq. 11):

$$\text{Water stable aggregate } (WSA) = \frac{W_a - W_c}{W_o - W_c} \times 100 \qquad (11)$$

where W_a is the weight of material on the sieve after wet sieving, W_c is the weight of sand particles, and W_o is the weight of aggregates placed on the sieve prior wet sieving.

Fractal dimension (D) is known as an index to evaluate the degree of crushing of large soil aggregates into smaller ones. Fractal dimension was calculated as one of the important indicators of the stability of soil aggregates by weighing the aggregates left on each sieve and using the following equation (Tyler and Wheatcraft, 1992) (Eq. 12):

$$\frac{M(x < X_i)}{M_T} = (\frac{X_i}{X_{max}})^{3-D} \quad (12)$$

where, X_i is the diameter of the i size aggregate and the X_{max} is the diameter of the largest aggregate in the sieve series. M(x < Xi) represents the cumulative weight of aggregates smaller than Xi in the sieve series, and M_T indicates the total aggregates left on the sieve series. D is the fractal dimension.

With transferring equation (4) in logarithmic form, the calculation of D relies on the following equation (Eq. 13):

$$log\left[\frac{M(x < X_i)}{M_T}\right] = (3 - D)\, log(\frac{X_i}{X_{max}}) \quad (13)$$

2.4.5. Heavy metal immobilization

To explore the applicability of pristine and modified biochars in heavy metal absorption, a batch experiment using biochar (different in origin of feedstocks and temperatures) was conducted. In general, sorption isotherms of zinc (Zn), copper (Cu), and cadmium (Cd) were determined using batch experiments in vitreous vials at room temperature (25 °C). The concentration of Zn^{2+}, Cu^{2+} and Cd^{2+} varied from 0 to 250 mg L^{-1}. After shaking for 24 h, and the final suspensions were centrifuged, filtered, and the supernatant solution was separated for analysis of Zn^{2+}, Cu^{2+}, and Cd^{2+} using inductively coupled plasma-mass spectrophotometer (ICP-MS) (Agilent 7500a, USA) (Deng et al., 2020; Ding et al., 2016; Nie et al., 2019).

In detail, 0.03 g (±0.005) of each biochar was thoroughly mixed with 30 mL of each metal solution ($ZnCl_2$, $Cd(NO_3)_2$, and $CuSO_4$) at concentrations of 5, 10, 25, 50, 75, 100, 150, 200 and 250 mg L^{-1} (9 vials). The pH of the solution was adjusted to pH=5 with 0.1 mol L^{-1} HNO_3 and 0.1 mol L^{-1} NaOH. The bottles were shaken at 180 rpm and 25 ± 1 °C for 24 h and then centrifuged at 4000 rpm for 10 min. Approximately 2 ml of supernatant was extracted from each bottle using 0.22-mm polyether sulfone filters. The non-adsorbed Zn^{2+}, Cu^{2+}, and Cd^{2+} were assessed using Inductively Coupled Plasma Emission Spectrometry (ICP-OES).

Chapter 3: Results and Discussion

3.1. Published outputs

Some outcomes of this thesis have been published in peer-reviewed scientific journals. The following eight articles are embedded in the final thesis:

1. Ghorbani, M*., Amirahamdi, E. (2024). Insights into soil and biochar variations and their contribution to soil aggregate status – A meta-analysis. Soil and Tillage Research, 244, 106282. https://doi.org/10.1016/j.still.2024.106282 (Impact Factor: 6.1 / Q1).

2. Ghorbani, M*., Amirahamdi, E. (2024). Biochar and soil contributions to crop lodging and yield performance - A meta-analysis. Plant Physiology and Biochemistry, 215, 109053. https://doi.org/10.1016/j.plaphy.2024.109053 (Impact Factor: 6.1 / Q1).

3. Ghorbani M*, Konvalina P, Walkiewicz A, Neugschwandtner W.R, Kopecky, M., Zamanian K, Chen WH, Bucur D (2022). Feasibility of biochar derived from sewage sludge to promote sustainable agriculture and mitigate GHG emissions—A review. International Journal of Environmental Research and Public Health, 19(19):12983. https://doi.org/10.3390/ijerph191912983 (Impact Factor: 4.6 / Q1).

4. Ghorbani, M*., Konvalina, P., Neugschwandtner, R.W., Kopecký, M., Amirahmadi, E., Walkiewicz, A., Bucur, D. (2022). Interaction of biochar with chemical, green and biological nitrogen fertilizers on nitrogen use efficiency indices. Agronomy, 12(9):2106. http://dx.doi.org/10.3390/agronomy12092106 (Impact Factor: 3.7 / Q1).

5. Ghorbani M*, Neugschwandtner RW, Konvalina P, Asadi H, Amirahmadi E (2022). Comparative effects of biochar and compost applications on water holding capacity and crop yield of rice under evaporation stress: a two-year field study. Paddy and Water Environment, 21: 47–58. https://doi.org/10.1007/s10333-022-00912-8 *(Impact Factor:2.2 / Q2)*

6. Ghorbani, M*., Konvalina, P., Kopecký, M., Kolář, L. (2022). A meta-analysis on impacts of different oxidation methods on surface area properties of biochar. Land Degradation and Development, 13(16):1-14. http://dx.doi.org/10.1002/ldr.4464 *(Impact Factor:3.7 / Q1)*

7. Ghorbani, M*., Neugschwandtner, R.W., Soja, G., Konvalina, P., Kopecký, M., (2023). Carbon fixation and soil aggregate formation affected by biochar oxidized with hydrogen peroxide: considering different pyrolysis temperatures and type of feedstocks. Sustainability, 15(9):7158. https://doi.org/10.3390/su15097158 *(Impact Factor:3.7 / Q2)*

8. Ghorbani, M*., Konvalina, P., Neugschwandtner, R.W., Soja, G., Barta, J. Chen, W.H. Amirahmadi, E (2024). How do different feedstocks and pyrolysis conditions effectively change biochar modification scenarios? A critical analysis of engineered biochars under H2O2 oxidation. Energy Conversion and Management, 300:117924. https://doi.org/10.1016/j.enconman.2023.117924 (Impact Factor:10.4 / Q1)

3.2. Role of biochar in soil properties

Stable feedstocks, such as wood or straw, have greater potential for forming soil aggregates since they include a higher percentage of decomposition-resistant components, such as cellulose and lignin, in their structure(Ghorbani et al., 2024; Han et al., 2021). Hydrocarbon polymer-containing feedstocks are particularly capable of creating a porous structure in biochar during the pyrolysis process (Brewer et al., 2014). This circumstance is critical for soil improvement since wood and straw-derived biochars have a large specific surface area and high porosity, which enhances their capacity to absorb and retain organic matter in the soil (Asadi et al., 2021; Suliman et al., 2017). Maintaining the soil's organic matter higher causes the soil's aggregation to rise because of the organo-mineral connections that occur between soil particles and biochar (Ghorbani et al., 2019; Yang et al., 2021). Additionally, beneficial conditions for the development of mycelium activities are provided by the high C/N ratio found in stable biomasses (Maaz et al., 2021; Wang et al., 2017; Zhan et al., 2021). The remaining lignocellulosic compounds in wood and straw biochars are broken down into fine, digestible molecules by mycelium, which secretes certain enzymes (Rouches et al., 2016; Taskin et al., 2019). This creates ideal circumstances for the association of soil and biochar particles (Jin et al., 2022; Mickan et al., 2016) and makes a substantial contribution to the macro aggregate's increase. Therefore, the considerable lignocellulosic compounds found in wood and straw biochar are responsible for the large percentage of macroaggregate formed in both, with the relative superiority of wood over straw. Consequently, the number of micro-aggregates will inevitably decrease as mycelial networks grow and larger macro-aggregates are formed from smaller particles and aggregates (Jien and Wang, 2013).

The primary contributing factor in the development of the final structure of biochar, after feedstock type, is the temperature during pyrolysis. In general, the aggregation conditions of soil can be significantly improved by raising the pyrolysis temperature (Islam et al., 2021). High pyrolyzed biochar's efficiency can be explained through two main mechanisms. First, the high-temperature-produced biochar has a lower molar ratio of O/C and becomes extremely hydrophobic (Ghorbani et al., 2023c; Lei and Zhang, 2013). Since biochar keeps the organic materials entrapped in its structure from dissolving, its hydrophobicity considerably lessens the dispersion of soil aggregates (Grunwald et al., 2016; Ma et al., 2024). This, in turn, greatly enhances the organo-mineral interactions that bind soil particles to biochar surfaces. It has been demonstrated that biochar created at temperatures higher than 500 °C was more hydrophobic than biochar produced at 300–500 °C, and the latter was also far more effective in preventing soil erosion (Gholamahmadi et al., 2023). It is obvious that the development of macro-aggregate, which is brought about by the strengthening of the organo-mineral interactions between soil particles and biochar, increases the soil structure's longevity and lowers the soil erodibility index (Franzluebbers, 2022; Heikkinen et al., 2019). This explains why there is a larger effect size related to the amount of macroaggregate formed in soils treated with high-pyrolyzed biochars. Also, our meta-analysis's findings further support the concept that biochar's hydrophobicity contributes to strengthening the soil structure, as shown by the positive correlation of the pyrolysis temperature and GMD with the erodibility index (K_e) (the paper in progress). On the other hand, the major effect size of micro-aggregates in soils treated with biochar generated at <450 °C accurately signifies the weakening of organo-mineral bonds and the dispersion of soil aggregates, ultimately preventing the formation of macro-aggregates. Second, the primary mechanism for absorbing and retaining nutrients on the surface of biochar is the presence of a broad variety of functional groups, particularly oxygenated functional groups such as carboxyl and hydroxyl onto the surface of biochar which has been pyrolyzed at a high temperature (Ghorbani et al., 2024). Additionally, biochar's large specific surface which has a high diversity of functional groups, it provides a sufficient substrate for microbial activity specially development of hyphae networks (Dai et al., 2018). This leads to more convergence of soil and organic particles and the formation of soil aggregates (Chen et al., 2021). According to our meta-analysis's findings, the biochar produced at various temperatures showed a positive effect size on WSA without significantly differing from each other. However, WSA cannot be directly impacted by the temperature of pyrolysis, even though it was higher at <450 °C since it contains less macro-aggregate than at higher temperatures.

3.3. Effect of biochar on plant productivity

Biochar's effectiveness in plant productivity notably depends on its application strategy. It has been reported that adding biochar and animal manure to the soil, improves the plants' ability to absorb nutrients and perform photosynthesis, resulting in an improvement in plant growth, which assess in increasing the yield (An et al., 2016; Zafar-ul-Hye et al., 2019). Also, it has been demonstrated that the soil volumetric water level rose up in biochar-manure combination in comparison with solely application of biochar which effectively can make change in sugar beet yield (Lebrun et al., 2022). Nevertheless, the quality assessment of sugar products revealed a positive contribution of biochar, more effective than cattle manure and conventional fertilization. Based on the results, the highest sugar content (SC) in both cultivation times was obtained from B15-treated fields with an average content of 16.6%. While application of cattle manure in all its rates, significantly decreased the percentages of SC compared with conventional fertilization, the same results were obtained for one ton of sugar yield (SY) per ha^{-1}. In sugar beet production, the sugar yield is inversely related to root yield (Lehrsch et al., 2015).

On the other hand, Biochar porous structure and developed specific surface area are two crucial factors that can notably affect water and nutrient availability in a biochar-treated soil, and it consequently results in the nutrient status of plant yield. The macro and micro-porous structures of biochars have previously been shown to advantageously impact soil moisture retention (Adekiya et al., 2019; Wang et al., 2019). In detail, the infrared analysis revealed that biochar surfaces had OH and C-O-H functional groups, on which nutrients bonded directly through polar interaction (Ghorbani et al., 2024). In addition, biochar can indirectly increase soil water content by improving soil structure, through bulk density reduction and aggregation stability improvement (Bohara et al., 2019; Wang et al., 2019), as well as the addition of organic carbon, which is known to increase soil water retention (Jačka et al., 2018).

In soils that are unable to retain nutrients and water, having a porous bulk with a well-developed surface area is essential for plant growth (Zi et al., 2023). As a result, adding biochar derived from straw—rather than biochar derived from wood—could be more effective since it supplies nitrogen and other macronutrients that are crucial for plant growth (Asadi et al., 2021). Several studies have shown that fundamental changes in the physicochemical structure of biochar, including a decrease in volatility, an increase in micropores, an expansion of the specific surface area, and an increase in several functional groups such as carboxyl and hydroxyl, occur as the pyrolysis temperature rises (Bayoka et al., 2023; Ghorbani et al., 2024; L. Li et al., 2023). As a result, these alterations improve biochar's ability to absorb cations and release cations such as ammonium that are essential for plant growth. It is obvious that plant function can be significantly impacted by applying a higher amount of biochar. Previous research demonstrated that biochar improved plants' key nutrient NPK absorption, increasing biomass output (Chew et al., 2020). However, it has been noted that applying biochar excessively may immobilize soil nitrogen, which could negatively impact crop growth and yield (B.-B. Li et al., 2021).

High application rate of biochar caused a notable increase in plant productivity and lodging resistance. It has been shown that the soil treated with biochar has a higher capacity for cation exchange owing to its high specific surface (Hailegnaw et al., 2019). Due to its porous nature, biochar facilitates the growth and habitation of a broad range of microorganisms that break down organic molecules, hence fostering the availability of nutrients for plant roots. Using more biochar increases the potential for microorganism growth and development resulting in plant productivity. It has been reported that applying rice husk biochar at a rate of 30 t ha^{-1} can dramatically enhance rice biomass output by up to 29% (Miao et al., 2023). Additionally, previous investigations have shown that biochar improved rice's absorption of the key nutrients—nitrogen, phosphate, potassium, and iron—which raised biomass output (Chew et al., 2020; Li et al., 2015). Rice biomass was shown to have significantly risen because of the biochar-rhizosphere interaction, which was claimed to have raised the membrane potential difference between the soil and the root. This, in turn, decreased the free energy needed for root nutrient accumulation (Chew et al., 2022).

Undoubtedly, along with the processes involved in producing biochar, the treated soil's inherent qualities determine the biochar's maximum efficiency in terms of crop productivity. It is well known that soil pH is controlled by the leaching of basic cations such as Ca, Mg, K, and Na far beyond their release from weathered minerals, leaving H^+ and Al^{3+} ions to dominant exchangeable cations (Neina, 2019). Most cereals which are matters in terms of crop resistance to lodging are plannable in alkalic soils (Lipiec and Usowicz, 2018; Nadeem et al., 2019). The physiologic characteristics of plants are directly influenced by the availability of alkalic cations in soil. It has been reported that cell wall components of growing regions could be strengthened due to tighter binding of Na^+ and Ca^{2+} that helps to mitigate cell loosing and maintain plant growth (Byrt et al., 2018). On the other hand, it is worth noting that biochar has an alkalic nature due to having a high cation exchange capacity (Fidel et al., 2017; Ghorbani et al., 2016). Therefore, the application of biochar could positively assess to increase in the availability of alkalic cations for plant roots. According to one of our meta-analysis's findings (in the process), plant quality, crop yield, and lodging resistance could all be improved by the availability of macronutrients. Enhancing grain yield and quality is mostly dependent on the availability of nitrogen in the soil. Regarding nitrogen's function in plant lodging resistance, it's important to note that nitrogen promotes assimilate formation in plant kernels following the silking stage, which in turn improves kernel setting and increased yield (Ning et al. 2018; Zhao et al. 2019). Also, as starch accounts for about 70% of the dry weight of grain, the amount of starch accumulation in grain determines its weight (X. Liu et al., 2021). It has been reported that nitrogen is particularly important for reducing the amount of amylose in grains and increasing the amount of protein and starch (Singh et al., 2011). Nonetheless, several investigations suggest that further research on plant productivity is needed to boost the prediction of the optimal available N that maximizes both plant productivity and environmental sustainability (X. Liu et al., 2021; Ordóñez et al., 2021; C. Wang et al., 2020). It has been observed that with increasing N fertilizer rate under water-limited field experiments, a reduction in root mass is expected (Ordóñez et al., 2021; Sun et al., 2020).

3.4. Effect of modification techniques on CEC of biochar

In terms of CEC, of all the alteration techniques, the soil mineral modification technique had the highest efficiency in terms of CEC. The enhanced capacity of soil minerals in the gradual abiotic oxidation of functional groups on the surface of biochar may account for the increased number of ion exchange sites seen in modified biochar (Mukherjee et al., 2014). The results of FTIR and XPS analysis in the literature, which demonstrates relative increases in oxygenated functional groups, such as substituted aromatic, carboxyl, and carbonyl C, confirm the role of oxidation in raising the surface acidity and CEC of the biochars (Ghorbani et al., 2024). It has been shown that the presence of amide was crucial in elevating the cation exchange sites in aged biochar when it came into contact with soil minerals (Hailegnaw et al., 2019). The direct precipitation of minerals on the surface of biochars is thought to be the second explanation. Numerous time-dependent environmental activities, often referred to as "aging," such as biotic and abiotic redox reactions, solubilization, and interactions with microorganisms, minerals, and solutes, can change the chemical structures of biochar. Therefore, as a result of the surface positive charge disappearing and the surface negative charge forming, these changes were followed by increases in the CEC of biochar (Cheng et al., 2008).

According to the data meta-analysis, acidic compounds performed effectively in raising CEC as well. Acid solutions cause pore-blocking substances on the surface of the biochar to dissolve, opening microscopic interior pathways for rapid penetration inside the biochar structure. The main environment for producing CEC, the micropores, eventually have a larger volume due to this process (Amin et al., 2020). Higher concentrations of acidic chemicals in treatments are associated with increased oxygenation of the biochar, mostly in the form of carboxyl groups (Mia et al., 2017). Carboxyl groups have an overall negative charge and are rather acidic in basic or neutral aqueous conditions, which makes them ideal for interactions with cations (Huff and Lee, 2016). On the other hand, an increase in surface carboxyl and hydroxyl groups may also account for the increased CEC of biochar modified by alkalic substances. The efficacy percentage is not quite the same, though. According to reports, biochar's surface area can significantly increase with KOH modification, bringing it comparable to commercial activated carbon (Liu et al., 2013). Also, it has been demonstrated that raising the level of alkaline oxides in the modification process of biochar can remove easily soluble cations (such as K^+ and Ca^{2+}), salts, carbonates, and silicates from the surface of biochar and prevent CEC increment (Zheng et al., 2021). According to the literature, the more frequently utilized metal oxides agents in biochar modification, are Fe_2O_3, Fe_3O_4, y-Fe_2O_3, and FeO (Gao et al., 2023; Mei et al., 2021) which are considered Fe oxides with high intrinsic CEC ranging from 61.4 to 219 mmol kg^{-1}. Therefore, the considerable rise in the CEC of modified biochar may be explained by the effectiveness of metal oxide alteration to achieve high CEC values in modified biochar.

It should be noted that when the pyrolysis temperature increases, the CEC of the biochars could drop due to the loss of many acidic functional groups at high temperatures (Janu et al., 2021). Furthermore, as a result of high ash content biochar created from easily biodegradable feedstocks such as straws, a high CEC is expected rather than wood-based biochar (Ghorbani et al., 2024). This outcome lends credence to the idea that the CEC value in biochar derived from herbaceous and straw are higher than that in biochar derived from wood.

3.5. Effect of modification techniques on atomic ratios of biochar

It is widely accepted that during the modification process of biochar, surface unstable carbon structure notably decomposes (Nie et al., 2019). Thus, carbon destruction and oxygen introduction result from biochar mineralization, which starts at the surface and continues through the modification process, increasing the O/C and H/C ratios (Kumar et al., 2022). According to reports, during the biochar modification process, oxidation produces ten oxygen compounds for every carbon that goes away (Yuan et al., 2020). It indicates that during the modification procedure, the surface C and O contents of the biochars would noticeably decrease and increase, respectively. Furthermore, it shows once again that the oxidizing activity of biochar was caused by two processes: the loss of aliphatic C and the rise of OFGs (Usman et al., 2015; Van Hien et al., 2020). On the other hand, it was shown that the surface of modified biochar with HNO_3 and H_2SO_4 produced somewhat more carboxyl and phenolic groups than the surface of modified biochar with H_2O_2, most likely because of a higher degree of oxidation (He et al., 2023; Wang et al., 2023). Furthermore, it has been reported that, in contrast to biochar that has been treated with NaOH, the application of HNO_3 and H_2SO_4 significantly affects the formation of oxygen groups on the surface of modified biochar (Fan et al., 2018; Ghorbani et al., 2023a). Considering biochar's organic carbon dissolves quickly in acid after modification, lowering the substance's C concentration, this could also be the cause of the acidic agent's greater efficiency compared to other types of modification substances (Lonappan et al., 2020).

Our findings demonstrated that the feedstock and pyrolysis temperature had a direct impact on the elemental composition of the biochars, as indicated by the molar ratios of C/N, H/C, and O/C in atomic measurements. It has been recognized that during the pyrolysis process, the unstable, amorphous structure of biomass is changed into a unified, stable structure of biochar known as the carbon skeleton (Chen et al., 2017). The O and H levels fall as the pyrolysis temperature rises since during the process, the amount of moisture and other oxygenated compounds that make up a significant portion of biomass diminish (Bakshi et al., 2016). As mentioned earlier, O/C and H/C ratios stand for the polarization and hydrophobic potential of biochar. These demonstrate the increasing carbonization and destruction of biomass during the pyrolysis process. Lower levels of these ratios suggest more aromatic chemicals and less polarity (Tian et al., 2022). Our findings showed that as the pyrolysis temperature increased, the atomic ratios of O/C and H/C in the modified biochars fell, indicating a decrease in polarity and an increase in aromaticity. The stability of modified biochar with low C/N is anticipated to be impacted by feedstocks having an inherent higher degree of degradability, such as manure and herbaceous materials (Ghorbani et al., 2024). Because of their low carbon skeleton and high water content, these readily decomposable feedstocks can also result in greater H/C and O/C ratios (Liang et al., 2023). For this reason, the C/N ratio was larger, and the H/C and O/C ratios were lower in the wood and nuts-based feedstocks.

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3.6. Effect of modification techniques on absorption characteristics of biochar

Porosity and specific surface area of biochar should be regarded as critical factors since they impact changes in other properties of biochar (Muzyka et al., 2023; Venkatachalam et al., 2023). However, acidic agents perform better than other modification agents because of their significant oxidation potential and high capacity to be integrated into the structure of biochar. In general the mineralization of biochar is greatly influenced by the surface (Bayoka et al., 2023). As mentioned earlier, the process of biochar mineralization starts at the surface and continues until carbon is depleted and oxygen is included (Akhil et al., 2021; Byambaa et al., 2024). During the modification process, the biochar's structure will undergo lengthwise wrinkles that will cause the volume of micropores to expand (Yan et al., 2020). Conversely, alkalic agents might have rapidly released too much oxygen, which would have wrecked the microstructure of the biochar and resulted in bigger pores (Liu et al., 2020; Shin et al., 2020). In the case of soil mineral efficiency, it has been discovered that clay particles relocate the biochar's internal pores and reduce the volume of micropores by clogging them (Ren et al., 2018). Moreover, the surface coating and specific surface area reduction of biochar are largely attributed to soil microorganisms (Cao et al., 2019). It has been shown that the metal oxide modification will cause biochar micropores to fill and reduction of SSA (Zhao et al., 2021). The physical modification did not significantly alter SSA, but it did exhibit a positive effect size. According to reports, the oxidation of biochar using steam creates pores and surface areas that greatly aid in the absorption of pollutants (Kumar et al., 2022). Additionally, the synthesis of sustainable skeletal carbon will be disrupted during low-heat pyrolysis due to the presence of volatile matter that blocks oxide agents from dispersing into the interior spaces of biochar. Consequently, the specific surface area of biochar could not be enhanced (Dhar et al., 2022). The biochar pores and the surface disparity both significantly expanded when the pyrolysis temperature got close to 500 °C. This could explain why the BD showed the lowest effect size while the SSA and TPV showed the largest increase in temperatures above 550 °C. Particles of ash content can significantly cause pore obstruction, which lowers biochar's absorption capacity (Oginni and Singh, 2020). Considering this, herbaceous and manure-based feedstocks with inherent high ash content result in low pore volumes and surface area.

The meta-analysis of both XPS and Bohem results (in process) confirms the positive effect size of modifications on oxygen functional groups of modified biochar including carboxyl (-COOH), hydroxyl (-OH), and carbonyl (C=O). Of all the modification agents, acidic modification displayed the largest OFG effect size. Higher concentrations of acidic chemicals have been observed to be associated with increased biochar oxygenation, predominantly demonstrated by carboxyl groups in acid-treated biochar (Lonappan et al., 2020; Lu et al., 2021). A range of OFGs are produced on the surface of the biochar as a consequence of acid treatments dissolving pore-blocking substances on the surface and opening microscopic channels inside for quick dispersion into the interior structure (Niu et al., 2023; Panwar and Pawar, 2022). to reports, CO- and -OH radicals were produced because of C-OH bound to biochar undergoing H_2O_2 oxidation through a single electron transfer pathway (Ghorbani et al., 2024). Also, strong peaks corresponding to the -COOH, -OH, and C=O functional groups following alteration are confirmed by the results of FTIR spectra of biochar treated with H_2O_2 in another investigation. Moreover, the modification of biochar using strong chemicals, such as acids and alkalis, results in additional procedures to remove remnants from the activated biochar, which increases the cost of the procedure, and the amount of water used. However, it has been demonstrated that few residues are left after the end of the reaction between biochar and H_2O_2. It shows that the

H_2O_2 modification could be considered as a relatively economical and environmentally beneficial method (He et al., 2022). Worth to note that, a few remnant H_2O_2 remain on the surface of biochar after use since most H_2O_2 ultimately may dissolve into O_2 and H_2O, which are both clean products (Tan et al., 2019; Xiaoying Zhang et al., 2020).

3.7. Conclusion

This work offers a thorough analysis of how various pyrolysis settings, types of feedstocks, and biochar modification methods could play effectively in the biochar's physicochemical characteristics. By methodically evaluating the effectiveness of various biochar modification procedures, this study fills a significant gap in the literature and contributes to the optimization of biochar for uses in environmental management and agriculture. The findings indicate that the efficiency of modification methods closely interacts with the range of pyrolysis temperature and feedstock degradability. Numerous characteristics of biochar are impacted by the alteration process, but the specific surface area, porosity, and oxygen functional groups—particularly carboxyl—are the main variables driving further modifications. These variables fundamentally contribute to most of the variations amongst various kinds of modified biochar. Meanwhile, acidic agents give the modified biochar a high absorption capacity and a porous carbon structure free of ash impurities because of their strong oxidation power and low ash content. The development of this porosity and specific surface area is aided using biochar that is formed at high pyrolysis temperatures. Also, biochar made from feedstock that is strong in lignin and low in volatile materials—such as wood, nuts, and straw—acts as an additional boosting factor to improve the absorption capabilities of biochar. Overall, understanding the variables that influence biochar's effectiveness and its qualities during modification procedures can be very beneficial to achieving the best biochar treatments in terms of managing various kinds of agricultural and environmental issues. A multi-aspect investigation of biochar production, modification, and application is provided by this work, covering a range of pyrolysis temperatures, and feedstock kinds that could help comprehend the complex nature of biochar and its applicability for soil amendment and pollution management due to its versatile attributes such as specific surface area, cation exchange capacity, and oxygen functional groups.

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List of Abbreviations

EC: electric conductivity

CEC: cation exchange capacity

O/C: oxygen to carbon ratio

H/C: hydrogen to carbon ratio

C/N: carbon to nitrogen ratio

MC: moisture content

VM: volatile matter

AC: ash content

FC: fixed carbon

BD: bulk density

SSA: specific surface area

TPV: total pore volume

PV_{micro}: micro-pore volume

PV_{meso}: meso-pore volume

APD: average pore size

OFGs: oxygen functional groups

N: nitrogen

P: phosphorus

K: potassium

List of Publications

45. **Ghorbani M*** and Amirahmadi E (2024). Insights into the catalytic capability of biochar affected by modification methods - A meta-analysis. *Journal of Environmental Chemical Engineering, 00*(0):0000. UNDER REVIEW | **Q1, IF:7.4**

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43. **Ghorbani M***, Amirahmadi E, Neugschwandtner RW (2024). Adsorption behavior of Cd, Cu, and Zn affected by pristine and H_2O_2-modified biochar. *Bioresource Technology, 00*(0):0000. UNDER REVIEW | **Q1, IF:9.7**

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41. Amirahmadi E*, **Ghorbani M**, Hörtenhuber SJ, Bernas J, Moudry J. Neugschwandtner RW, Krexner T, Konvalina P (2024). Life cycle assessment of biochar and cattle manure application in sugar beet cultivation – Insights into root yields, white sugar quality, environmental aspects in field and factory phases. *Journal of Cleaner Production, 00*(0):0000. UNDER REVIEW | **Q1, IF:9.7**

40. Walkiewicz A*, Kubaczyński A, Rafalska A, **Ghorbani M**, Osborne B (2024). Temperature sensitivity of respiration in biochar-amended soils with different textures and fertilizer treatments. *Scientific Reports, 00*(0):0000. UNDER REVIEW | **Q2, IF:4.6**

39 **Ghorbani M*** and Amirahmadi E (2024). Insights into soil and biochar variations and their contribution in soil aggregate status - A meta-analysis. *Soil and Tillage Research,* 244:106282. https://doi.org/10.1016/j.still.2024.106282 | **Q1, IF:6.1**

38 Bernas J*, Hoang TN, **Ghorbani M**, Amirahmadi E, Shahzaib A, Baloch SB, Murindangabo TG, Konvalina P, Bernasova T, Nedbal V (2024). Hotspot detection in the cultivation of organic winter wheat variety mixtures. *The International Journal of Life Cycle Assessment*, 00(00):0000. https://doi.org/10.1007/s11367-024-02360-4 | **Q1, IF:4.9**

37 **Ghorbani, M*** and Amirahmadi E (2024). Biochar and soil contributions to crop lodging and yield performance - A meta-analysis. *Plant Physiology and Biochemistry,* 215:109053. https://doi.org/10.1016/j.plaphy.2024.109053 | **Q1, IF:6.1**

36 Bernasova T*, Nedbal V, **Ghorbani M**, Brom J, Amirahmadi E*, Bernas J (2024). Eutrophication Risk Potential Assessment between Forest and Agricultural Sub-Catchments Using LCIA Principles. *Land*, 13(8):1150. https://doi.org/10.3390/land13081150 | **Q2, IF:3.2**

35 Chang MH, Chen WH*, Wu DR, **Ghorbani M**, Rajendran S, Daud WM (2024). Optimization of hydrogen purification from biomass-derived syngas via water gas shift reaction integrated with vacuum pressure swing adsorption for energy storage. *Energy Conversion and Management: X*, 23:100645. https://doi.org/ 10.1016/j.ecmx.2024.100645 | **Q1, IF:7.1**

34 Hoang TN*, Konvalina P, **Ghorbani M**, Nguyen TG., Bernas J, Murindangabo TG, Shim S (2024). Assessing the quality and grain yield of winter wheat in the organic farming management under wheat-legume intercropping practice. *Heliyon*, 10(10):E31234. https://doi.org/10.1016/j.heliyon.2024.e31234 | **Q1, IF:3.9**

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20. Amirahmadi E*, **Ghorbani M**, Moudrý J, Konvalina P, Kopecký M (2023). Impacts of environmental factors and nutrient management on tomato grown under controlled and open field conditions. Agronomy, 13(3):916. https://doi.org/10.3390/agronomy13030916 | **Q1, IF:3.7**

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16. **Ghorbani M***, Amirahmadi E, Konvalina P, Moudrý J, Bárta J, Teodorescu RI, Bucur RD (2022). Comparative influence of biochar and zeolite on soil hydrological indices and growth characteristics of Corn (Zea mays L.). Water, 14(21):3506. https://doi.org/10.3390/w14213506 | **Q1, IF:3.4**

15. Amirahmadi E*, Moudrý J, **Ghorbani M** (2022). Effects of Zeolite on aggregation, nutrients availability and growth characteristics of Corn (Zea mays L.) in cadmium-contaminated soils. Water, Air, & Soil Pollution, 233(436):1-12. https://doi.org/10.1007/s11270-022-05910-4 | **Q2, IF:2.9**

14. **Ghorbani M***, Neugschwandtner RW, Konvalina P, Asadi H, Amirahmadi E (2022). Comparative effects of biochar and compost applications on water holding capacity and crop yield of rice under evaporation stress: a two-years field study. Paddy and Water Environment, 21: 47–58. https://doi.org/10.1007/s10333-022-00912-8 | **Q2, IF: 2.2**

13. **Ghorbani M***, Konvalina P, Walkiewicz A, Neugschwandtner R, Zamanian K, Chen WH, Bucur D (2022). Feasibility of biochar derived from sewage sludge to promote sustainable agriculture and mitigate GHG emissions—A review. International Journal of Environmental Research and Public Health, 19(19):12983. https://doi.org/10.3390/ijerph191912983 | **Q1, IF: 4.614**

12. **Ghorbani M***, Konvalina P, Kopecký M, Kolář L (2022). A meta-analysis on impacts of different oxidation methods on surface area properties of biochar. Land Degradation and Development, 13(16):1-14. http://dx.doi.org/10.1002/ldr.4464 | **Q1, IF: 4.377**

11. **Ghorbani M***, Konvalina P, Neugschwandtner RW, Amirahmadi E, Walkiewicz A, Bucur D (2022). Interaction of biochar with chemical, green and biological nitrogen fertilizers on nitrogen use efficiency indices. Agronomy, 12(9):2106. http://dx.doi.org/10.3390/agronomy12092106 | **Q1, IF:3.7**

10. **Ghorbani M***, Konvalina P, Neugschwandtner RW, Amirahmadi E, Moudrý JJ, Menšík L (2022). Preliminary findings on cadmium bioaccumulation and photosynthesis in rice (Oryza sativa L.) and maize (Zea mays L.) using biochar made from C3- and C4-originated straw. Plants, 11(2):43. https://doi.org/10.3390/plants11111424 | **Q1, IF:4.5**

9. Kopecký M*, Kolář L, Perná K, Váchalová R, Mráz P, Konvalina P, Murindanbo T, **Ghorbani M,** Menšík L, Dumbrovský M (2022). Fractionation of soil organic matter into labile and stable fractions. Agronomy, 12(1):73. https://doi.org/10.3390/agronomy12010073 | **Q1, IF:3.7**

8. Nazari M*, Eteghadipour M, Zarebanadkouki M, **Ghorbani M**, Dippold MA, Zamanian K (2021). Impacts of logging-associated compaction on forest soils: A meta-analysis. Frontiers in Forests and Global Change, 4, 780074. https://doi.org/10.3389/ffgc.2021.780074 | **Q1, IF:3.2**

7. Asadi H*, **Ghorbani M**, Rezaei-Rashti M, Abrishamkesh S, Amirahmadi E, Chengrong CHEN, Gorji M (2021). Application of rice husk biochar for achieving sustainable agriculture and environment. Rice Science, 28(4), 325-343. https://doi.org/10.1016/j.rsci.2021.05.004 | **Q1, IF:4.8**

6. **Ghorbani M***, Amirahmadi E, Zamanian K (2021). In-situ biochar production in paddies: direct involvement of farmers in greenhouse gases reduction policies besides increasing nutrient availability and rice production. Land Degradation & Development, 32(14), 3893-3904. https://doi.org/10.1002/ldr.4006 | **Q1, IF:4.377**

5. Amirahmadi E, Hojjati SM, Kammann C*, **Ghorbani M,** Biparva P (2020). The potential effectiveness of biochar application to reduce soil Cd bioavailability and encourage oak seedling growth. Applied Sciences, 10(10), 3410. https://doi.org/10.3390/app10103410 | **Q2, IF:2.7**

4. **Ghorbani M***, Asadi H, Abrishamkesh S (2019). Effects of rice husk biochar on selected soil properties and nitrate leaching in loamy sand and clay soil. International Soil and Water Conservation Research, 7(3), 258-265. https://doi.org/10.1016/j.iswcr.2019.05.005 | **Q1, IF:6.4**

3. **Ghorbani M*** and Amirahmadi E (2018). Effect of rice husk Biochar (RHB) on some of chemical properties of an acidic soil and the absorption of some nutrients. Journal of Applied Sciences and Environmental Management, 22(3), 313-317. https://doi.org/10.4314/jasem.v22i3.4 | ISSN: 2659-1502

2. **Ghorbani M*** and Amirahmadi E (2018). Effect of rice husk biochar on some physical characteristics of soil and corn growth in a loamy soil. Iranian Journal of Soil Research, 32(3), 305-318. https://dx.doi.org/10.22092/ijsr.2018.117821 | **IF:0.078**

1. **Ghorbani M***, Asadi H, Abrishamkesh S (2016). Effect of rice husk biochar on Nitrate Leaching in a clayey Soil. Iranian Journal of Soil Research, 29(4), 127-434. https://dx.doi.org/10.22092/ijsr.2016.105902 | **IF:0.078**

Curriculum Vitae

Mohammad Ghorbani

Researcher in Soil Science and Biochar
Scopus-based H-index: 15

| Education

- **Doctor of Philosophy (Ph.D.)** in Plant Science, University of South Bohemia, Czechia, 2024.
- **Master of Science (M.Sc.)** in Soil Science, University of Guilan, Iran, 2015.
- **Bachelor of Science (B.Sc.)** in Soil Science, University of Guilan, Iran, 2013.

| Positions, Trainings, Internships

- **Visiting Scholar** at Ghent University, Belgium, September-October 2024.
  1) *Understanding of state-of-the-art techniques for soil-physical and soil-hydraulic characterization of soil (KSAT, HYPROP, EMI, ERT, GPR, …) and telemetric sensor-based monitoring of soil variables.*
  2) *Discussion and demonstration on the use of soil amendments, especially biochar to build resilience against drought: from lab to greenhouse to field.*
- **Visiting Researcher** at Geisenheim University, Germany, June-July 2024.

Attended the DAAD-funded summer school on agricultural greenhouse gas (GHG) flux measurement techniques, novel analytical methods, potential methodical, drawbacks and pitfalls, flux calculation, and upscaling/sum calculation protocols. Experienced in:

1) *Encompasses CO_2 footprint calculations according to the latest IPCC global warming potential considerations as a preparation for agricultural life cycle analysis.*
2) *Novel experimental approaches on agricultural tests of biochar and rock powder (enhanced weathering) as CDR techniques, alone and in combination (co-pyrolysis). Within the current BMBF-funded Network project "PyMiCCS" (pyrolysis and enhanced mineral weathering for carbon capture and storage) within the CDRterra Consortium.*
3) *Methodical use of a Picarro analyser employing the novel measurement technique CRDS 8cavity ring-down spectroscopy) for gaseous stable Carbon isotope measurements and their application in agricultural ecology.*
4) *Soil acoustic measurement techniques for monitoring soundscapes below-ground as a tool to investigate belowground macrofauna biodiversity in soils.*
5) *State of the art knowledge of GHG flux measurement calculation methods (closed and dynamic chambers; different analytical methods and platforms and their operation modes), all of which also demand digital skills, due to different types of analyzers, software, and R protocols that have to be modified and used.*
6) *Use of R protocols for experimental block design statistics and graphics.*
7) *Use of the respective R protocols and R programming skills to put the newly acquired theory into research practice.*

- **Visiting Scholar** at the University of Milan, Italy, May 2024.

Experienced in the field of biosystems and bioresources management in agriculture at the Department of Agriculture and Environmental Science.

- **Visiting Researcher** at Aarhus University,
  Denmark, April 2024.

Experienced in novel methods to measure soil water retention in the dry region using pressure plate, Vapor Sorption Analyzer (VSA), CT scan imagery, ...

- **Fellow Researcher** at the University of Natural Resources and Life Sciences in Vienna,
  Austria, March 2024.

Leading a project aiming at the assessment of the adsorption capacity of pristine and modified biochar in the immobilization of heavy metals through ICP analysis.

- **Research Assistant** at the University of Helsinki,
  Finland, May-June 2023.

Experienced in:

1) *GHG sampling from the field with chamber method*
2) *Gas Chromatography measurements*
3) *X-ray diffractometry (XRD) analysis of biochar - PANalytical X Pert Pro.*
4) *TDR methods for soil moisture measurements*
5) *Drone running, setting plan with Pix4D, and analyzing the data for photosynthesis measurements.*

- **Visiting Scholar** at Charles University,
  Czechia, February 2023.

Experienced in:

1) *Elemental analyzer (Agilent /ICP-OES-5900)*
2) *FTIR spectrometer (Thermo Scientific /Nicolete)*
3) *Combined liquid and ion chromatography (Dionex ICS 5000+)*
4) *Gas chromatograph (Hewlett Packard 5890 Series II)*
5) *Atomic absorption spectrophotometer (Perkin Elmer 306)*
6) *Gas chromatography analysis (Thermo Scientific TRACE 1310 GC IsoLink II Interface-IRMS)*
7) *Isotopic composition of elements (Neptune Plus High-Resolution Multicollector ICP-MS).*

- **Researcher** at the University of Natural Resources and Life Sciences in Vienna,
  Austria, June-August 2022.

Experienced in:

1) *CHNS Elemental Analyzer (Leco 630.100.500)*
2) *FTIR-Fourier (Perkin Elmer Spotlight 400N)*
3) *Scanning electron microscope (SEM) imaging (Hitachi TM3030)*

4) *Vacuum Coater (Leica EM ACE200)*

5) *Electrical Muffle Furnace (Nabertherm N41/13)*

6) *Phenotyping with a high-resolution RGB camera mounted on a drone*

7) *Diversity in oats: winter versus spring sowing*

8) *Resistance research: resistance to stone blight in winter wheat*

9) *Smart assessment of wheat growth and photosynthesis (experienced in FieldSpec Handheld, Greenseeker, SPAD, PolyPen, AccuPAR, …).*

- **Firm Owner** in Rasht, Iran,
  Iran, June-August 2019.

A consulting company with aims of biochar production and integrating farmers to use their local agricultural wastes in a beneficial approach.

- **Project Manager** at Rice Research Institute of Iran and Guilan Science and Technology Park,
  Iran, 2018.

During my career, I conducted some field research projects focusing on the effects of biochar on rice productivity, heavy metal immobilization, and GHG emissions from paddy fields.

- **Quality Control Expert** at Tea Organization, Ministry of Agriculture
  Iran, 2018.

As a quality controller part of my responsibilities was giving advice to farmers in terms of proper development of drip irrigation, fertilizer management, and seasonal pruning of tea shrubs.

| Scholarships

- **Winner of faculty scholarship for abroad scientific mobility** ***(June 2022)***
  For mobility to the University of Natural Resources and Life Sciences in Vienna, Austria.
- **Winner of faculty scholarship for internal scientific mobility (February 2023)**
  For mobility to Charles University, Czechia.
- **Winner of faculty scholarship for abroad scientific mobility** ***(May 2023)***
  For mobility to the University of Helsinki.
- **Winner of ERASMUS+ higher education scholarship for scientific mobility** ***(March 2024)***
  For mobility to the University of Natural Resources and Life Sciences in Vienna, Austria.
- **Winner of ERASMUS+ higher education scholarship for scientific mobility** ***(April 2024)***
  For mobility to Aarhus University, Denmark.
- **Winner of ERASMUS+ higher education scholarship for scientific mobility** ***(May 2024)***
  For mobility to the University of Milan, Italy.
- **Winner of ERASMUS+ higher education scholarship for scientific mobility** ***(June 2024)***
  For mobility to Geisenheim University, Germany.

- **Winner of ERASMUS+ higher education scholarship for scientific mobility** ***(September 2024)***
  For mobility to Ghent University, Belgium.
- **GAJU-Project scholarship from the doctoral university** ***(2021- 2024)***
  For progress in the Ph.D thesis and achievements in scientific publication.

| Conferences

- **5th Global Food Security Conference in KU Leuven, Leuven, Belgium. 9th - 12th April 2024**
  Biochar for food security and GHG emissions mitigation. Insights into involving farmers in sustainable biochar production- challenges and opportunities.
- **3rd Conference of Doctoral Students in University of South Bohemia, České Budějovice, Czechia. 21st - 22nd November 2023**
  Characterization of oxidized biochar as a cost-effective absorbent and soil modifier.
- **2nd Conference of Doctoral Students in University of South Bohemia, České Budějovice, Czechia. 7th - 8th December 2022**
  A meta-analysis on the influence of oxidized biochar on crop yield.
- **8th International Conference on Trends in Agricultural Engineering, Czech University of Life Sciences, Prague, Czech Republic 20th - 23rd September 2022**
  Oxidation of biochar as a modification technique for boosting biochar benefits.
- **8th International Conference on Trends in Agricultural Engineering, Czech University of Life Sciences, Prague, Czech Republic 20th - 23rd September 2022**
  Wheat and legume mixtures influence grain quality.
- **15th Soil Science Congress of Iran, Isfahan, Iran. 28th - 30th August 2017**
  Effect of rice husk biochar on aggregate stability in two soil types of clay and loamy sand.
- **13th Soil Science Congress of Iran, Rafsanjan, Iran. 7th - 9th September 2015**
  Monitoring nitrate leaching in soil amended by biochar and compost.

| Teaching, Talks

- **At: Department of Agroecology - Soil Physics & Hydropedology, Aarhus University, Foulum, Denmark.**
  On: Prospects of modified biochars in agricultural soil functions. 2024.
- **At: Department of Agroecosystems, Faculty of Agriculture & Technology, University of South Bohemia, Ceske Budejuvice, Czechia**
  On: Biochar characterization for absorption purposes in soil. 2024.
- **At: Institute for Environmental Studies, Faculty of Science, Charles University, Prague, Czechia.**
  On: Boosting biochar benefits with oxidation modification techniques. 2023.
- **At: Institute of Agronomy, Department of Crop Sciences, University of Natural Resources & Life Sciences in Vienna, Austria.**
  Introduction of Meta-analysis on agricultural data sets. 2022.
- **At: Tea Organization of Iran, Ministry of Science Research & Technology of Iran.**
  Modification of intensive acidic soils in tea lands using biochar. 2020.
- **At: Rice Research Institute of Iran, Ministry of Science Research & Technology of Iran.**
  On: Reuse of rice residues for biochar production. 2018.

- **At: Guilan Science & Technology Park, Ministry of Science Research & Technology of Iran.**
  On: Potential of various types of feedstocks for producing biochar in simple ways by farmers according to the needs of the living area. 2017.
- **At: Department of Soil science, Faculty of Agricultural Sciences, University of Guilan, Iran.**
  On: Pyrolysis conditions and limitations for biochar production. 2015.
- **At: Department of Soil science, Faculty of Agricultural Sciences, University of Guilan, Iran.**
  On: Introducing biochar as a new soil amendment. 2014.

| Practical Research Experiences

- **Field & Greenhouse**
  Crop processing (Wheat, Rice, Canola, Maize, …) / Intercropping systems / Organic and conventional farming / GHG emission monitoring in crop fields / Soil and plant sampling / Nutrient leaching experiments / Heavy metal immobilization / Soil water content using TDR / nutrient cycling / Smart assessment of wheat growth and photosynthesis using FieldSpec Handheld, Greenseeker, SPAD, Poly-Pen, AccuPAR, ...
- **Laboratory**
  Spectrophotometry / Gas chromatography / Soil moisture analysis using pressure plate, Vapor Sorption Analyzer (VSA), and CT scan imagery / Batch experiments for heavy metal sorption / ICP-OES analyzer / FTIR / SEM / XRD / CHSNO analyzer / ...
- **Biochar**
  Biochar production in muffle furnaces using variety of temperatures and feedstocks/biochar characterization in basic and advanced analysis such as FTIR, Vacuum coater, SEM, XRD, ...
- **Software**
  SPSS / OriginPro / R / MetaWin / Microsoft Office.

| Professional Services

- **Journal Reviewer**
  Elsevier: Catena / Agricultural Water Management / Soil & Tillage Research / European Journal of Agronomy / Environmental Pollution / Environmental Technology & Innovation / Journal of Hazardous Materials / Agriculture, Ecosystems and Environment.
  Springer: Biochar / Journal of Soils and Sediments / Journal of Soils Science & Plant Nutrition / Environmental Geochemistry and Health.
  Nature: Scientific Reports / Biomass Conversion and Biorefinery / Clean Technologies and Environmental Policy
  Wiley: Land Degradation & Development.
- **Journal Editor**
  Special issue on Application of Biochar in Sustainable Soil Management: Challenges and Perspectives. Agriculture Journal – MDPI.
- **Book Translator**
  A book named Biocharculture by Dr. Sai Bhaskar Reddy was translated from English to Persian.