Universidade de Aveiro Departamento de Ambiente e Ordenamento
2020

Dina Jahanianfard

Aplicação de biochar no solo: efeitos e toxicidade

Biochar application in soil: behavior and toxicity

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Dissertação apresentada à Universidade de Aveiro para cumprimento dos requisitos necessários à obtenção do grau de Mestrado Integrado em Engenharia do Ambiente, realizada sob a orientação científica da Prof. Doutora Ana Paula Duarte Gomes, Professora Auxiliar do Departamento de Ambiente e Ordenamento da Universidade de Aveiro e do Doutor Mohammadreza Kamali, Assistente da Universidade de Ku Leuven.

Este trabalho foi realizado no âmbito das atividades do projeto "PROTEUS - Produtos e tecnologias para o setor de Eucalyptus globulus", com a referência POCI-01-0247-FEDER-017729, através do Fundo Europeu de Desenvolvimento Regional (FEDER) no âmbito do COMPETE - Programa Operacional de Competitividade e Internacionalização (POCI), Portugal

Dedico este trabalho aos meus amados pais, Fereshteh Omidolhagh e Morteza Jahanianfard, e também ao meu adorável marido, Amid Mostafaie, pelo apoio constante, que me permite perseguir meus sonhos.

o júri

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palavras-chave

biochar, cientometria, derivado de lama, incubação, fitotoxicidade, teste de germinação, teste de crescimento.

resumo

O biochar é um subproduto produzido a partir da pirólise de um substrato orgânico, principalmente biomassa, através de um processo termoquímico com presença limitada ou sem a presença de oxigénio. A aplicação do biochar remonta a aproximadamente 2000 anos atrás, sabendo-se que era praticado principalmente na antiga Amazónia. No sentido de poder contribuir para o conhecimento científico na área da aplicação do biochar como aditivo para o solo, foi realizado um estudo cientométricos na colecção central da Web of Science com a pesquisa prévia de algumas palavras-chave específicas e foi recuperado o número total de 2123 documentos em inglês, publicados entre 2000 e 2018. Esses registros bibliográficos foram analisados em relação a alguns critérios cientométricos, como tipo de publicação, ano de publicação, país contribuinte, análise de palavras-chave, análise de autores, autores citados, periódicos citados, categorias e documentos citados.Os resultados obtidos a este respeito demonstraram que, apesar de muitas investigações realizadas neste domínio, a necessidade de uma maior colaboração entre os investigadores a nível mundial e a superação das questões relativas à matéria-prima adequada, às condições de pirólise e ao comportamento tóxico do biochar, é ainda muito necessário, a fim de se chegar a comercializar a aplicação do biochar, como aditivo para o solo.

Como estudo de caso, um tipo de biochar foi produzido a partir da pirólise de lamas biológicas do tratamento das águas residuais da indústria da pasta e do papel. O biochar produzido foi analisado quanto às suas características químicas e físicas. A análise realizada revelou que o biochar era poroso e possuía uma microestrutura irregular. Também apresentou pH e condutividade eléctrica elevados.

Seguidamente, foi realizado um teste de incubação do solo incubado com o biochar como aditivo. Para proporcionar uma comparação, foi também aplicado um agente comercial de calagem em diferentes amostras de solo. As amostras de solo aditivadas com o agente de calagem também foram mantidas na incubação. Posteriormente, no período de incubação, que foi de 21 dias, observou-se que o biochar tem a capacidade de alterar o pH, a condutividade eléctrica e a capacidade de retenção de água do solo, enquanto com o agente comercial de calagem, apenas o pH aumentou significativamente, não tendo sido observadas alterações consideráveis nos outros parâmetros medidos. (continua na próxima página)

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palavras-chave

biochar, cientometria, derivado de lama, incubação, fitotoxicidade, teste de germinação, teste de crescimento.

resumo

Foi efectuada um ensaio de fitotoxicidade com germinação de sementes e o seu crescimento através da aplicação de sementes de *Lepidium sativum* (para o teste de germinação) e de sementes de *Lolium perenne* (para o teste de crescimento). Os resultados obtidos a este respeito demonstraram o efeito não tóxico da adição de biochar na germinação das sementes. Pela realização do ensaio de crescimento, observou-se que o biochar com a dose correspondente de 2,5% p/p aumentou significativamente o rendimento da cultura, em comparação com o solo tal qual recebido, permitindo obter plantas com maior altura foliar e maior peso seco. Embora a cultura obtida a partir do solo aditivado com as doses mais elevadas do biochar tenha tido um efeito negativo sobre o rendimento da cultura. O agente comercial de calagem também não aumentou significativamente o rendimento da cultura. No entanto, é considerado crucial para uma aplicação segura, uma investigação mais aprofundada sobre a absorção de elementos potencialmente tóxicos pelas plantas cultivadas em solo aditivado com o biochar.

keywords

biochar, scientometry, sludge-derived, incubation, phytotoxicity, germination test, growth test.

abstract

The biochar is a by-product produced from the pyrolyzing an organic feedstock, mainly biomass, through a thermochemical process with limited or without the presence of oxygen. The application of biochar goes back to approximately 2000 years ago knowing that it was practiced mainly in ancient Amazonia. In order to determine the growth of the science in the area of the biochar application as a soil additive, a scientometric study was performed in the Web of Science core collection with the advance search of some specific keywords and the total number of 2123 English documents were retrieved published from 2000 to 2018. These bibliographic records were then analyzed regarding some scientometric criteria such as publication type, publication year, contributing country, keyword analysis, author analysis, cited authors, cited journals, categories, and cited documents. The obtained results in this regard demonstrated that despite many research performed in this field, the need regarding more collaboration among the researchers globally and overcoming matters regarding the proper feedstock, pyrolysis condition, and toxic behavior of the biochar is still greatly felt in order to commercialize the biochar application as a soil amendment.

Moreover, as a case study, one type of biochar was pyrolyzed from the secondary sludge of the wastewater treatment of pulp and paper mill industry. Further, the produced biochar was analyzed regarding its chemical and physical characteristics. The performed analysis revealed that the biochar was porous and possesses an irregular microstructure. Also, it was in high pH and electric conductivity.

Further on, an incubation test was conducted on the soil incubated with biochar as the additive. To provide a comparison, a liming agent was also applied in different soil samples. The amended soil samples with the liming agent were also kept in the incubation. Thereafter the incubation period, which was 21 days, it was observed that the biochar has the capacity to alter the pH, electrical conductivity, and the water holding capacity of the soil while with the liming agent only the pH increased significantly and no considerable modifications were observed in the other measured parameters. (continues to the page)

keywords

biochar, scientometry, sludge-derived, incubation, phytotoxicity, germination test, growth test.

abstract

Furthermore, a phytotoxicity analysis regarding the germination of the seeds and their growth was conducted via the application of *Lepidium sativum* seeds (for germination test) and *Lolium perenne* seeds (for growth test). The obtained results in this regard demonstrated the non-toxic effect of the biochar addition on the seed germination. Also, thereafter the conduction of the growth test, it was observed that the biochar with the corresponding dose of 2.5% w/w enhanced the crop yield significantly in comparison to the collected soil via providing the crops with more dry-weight and height. While the crop obtained from the amended soil with the biochar higher doses had a negative effect on the crop yield. The liming agent did not significantly increase the crop yield as well. However, more research regarding the potentially toxic elements uptake by plants grown in the amended soil with biochar is considered to be crucial for a safe application of such an amendment.

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Nomenclature of chemicals

O_2	oxygen
C	carbon
CO_2	carbon dioxide
CH_4	methane
N_2O	nitrous oxide
N	nitrogen
Cl	chlorine
NH_4^+	ammonium
NO_3^-	nitrate
$HCL.H_2O$	hydrochloric acid
H_2SO_4	sulfuric acid
KCL	potassium chloride
$CaCO_3$	calcium carbonate
Ca	calcium
Na	sodium
K	potassium
P	phosphor
Cu	copper
Mg	magnesium
Fe	iron
Ni	nickel
Pb	lead
Zn	zinc
Al	aluminum
Cr	chromium
NH_4NO_3	ammonium nitrate
SiO_2	silicon oxide
$KAlSi_2O_6$	potassium aluminum silicon oxide
Cd	cadmium
Mn	manganese

Abbreviations and acronyms

ISI	international scientific indexing
WoS	Web of Science
BC	betweenness centrality
CB	citation burst
CC	citation count
CF	citation frequency
VOCs	volatile organic compounds
R&D	research and development
GHG	greenhouse gases
CEC	cation exchange capacity
EC	electrical conductivity
WHC	water holding capacity
PAHs	Polycyclic aromatic hydrocarbons

wb	wet basis
SSA	specific surface area
XRD	X-ray powder diffraction
SEM	Scanning electron microscope
EDX	Energy-dispersive X-ray spectroscopy
XRF	X-ray fluorescence spectroscopy
ICP-MS	Inductively coupled plasma mass spectrometry
TOC	total organic carbon
TIC	total inorganic carbon
ISO	international organization for standardization
Mol/L	mole/Liter
w/v	weight/volume
G%	germinated seed percentage
L%	root length percentage
GI%	germination index percentage
db	dry basis
BET	Brunauer, Emmett and Teller
Å	ångströms

Nomenclature

wb [%]	(weight of water/weight of wet solid)
adsorbed/desorbed	mmol/g
Brunauer, Emmett and Teller area	m^2/g
Pore volume	cm^3/g
Pore size	Å or nm
Nitrate content	g NO_3^-/ kg biochar
Chlorine content	%
Carbon content	g C/kg biochar
Electrical conductivity	mS/cm or μS/cm
Crop height	cm
Crop weight	g

General Introduction

The biochar is a soil amendment that is produced when a biodegradable feedstock goes through a thermal process of being heated from 300°C to 700°C without and/or with limited presence of oxygen (Wu *et al.*, 2017). This thermal process is called the pyrolysis (Alghamdi, 2018) and the produced biochar is also known as a pyrolysis product, charcoal, and black carbon (Rajapaksha *et al.*, 2015). The characteristics of the produced biochar are highly dependent on the utilized feedstock (Głąb *et al.*, 2018) and the pyrolysis conditions (Nguyen *et al.*, 2017) applied during the production. Previously, the main feedstocks used for the purpose of biochar production were agricultural wastes, agricultural products, animal bones, and animal manures (Liu *et al.*, 2018). However, due to the interfere of the application of such feedstocks with the production of biofuels and also with the food industry, the application of such feedstocks has lost their attractions (Laird *et al.*, 2009). Consequently, other types of feedstocks such as municipal wastes and the sludges produced from the treatment of different kinds of wastewaters, whether municipal and/or industrial, have been recently gained popularity to be utilized as the feedstock for the biochar production (Mousavi, Moshiri and Moradi, 2018). Moreover, the applied conditions as the maximum temperature, the rate of achieving the highest temperature, and the residence time, i.e. the amount of the time that the feedstocks is left in the maximum applied temperature, also play a crucial role in the properties of the obtained biochar (Břendová *et al.*, 2017). The properties varying due to different types of feedstocks and the pyrolysis conditions mainly affect the corresponding chemical and physical characteristics of the produced biochar like its corresponding ash and consequently carbon content, its pH (Lehmann *et al.*, 2011), its electrical conductivity (EC) (Ojeda *et al.*, 2015), its water holding capacity (WHC) (Laird *et al.*, 2009), its microstructure (Jien *et al.*, 2015), its porosity (Jaafar, Clode and Abbott, 2015), its surface area (Lehmann *et al.*, 2011), etc. However, due to different types of biochar applied recorded in the literature, there is still uncertainty regarding the safe application of such a product as a soil amendment, and the need for more research regarding the application of the biochar as a soil additive is still greatly felt.

The application of the biochar goes back as far as 2500 years ago as in our best knowledge was primarily practiced by the ancient Amazonians. This practice has led to a highly fertile soil which is called "black earth" and with the original name of "terra preta" in Portuguese. The performed analysis on this soil revealed that the amount of its corresponding organic content must be anthropogenic and has been caused by the addition of biochar which was produced from fish bones and animal manures (Laird et al., 2009). Thus, in order to mark the growth of the knowledge and the corresponding trends in the application of such a soil amendment, a scientometric study is accounted to be beneficial (Konur, 2012). In order to proceed with this study, Web of Science (WoS) core collection was adapted as the main database. Thereafter the execution of research, the relevant keywords were retrieved and were inserted in the above-mentioned database for further analysis. The obtained results demonstrated that the total number of 2123 documents have been published in this regard between 2000 to 2018. Further on, the extracted documents were analysed regarding some of the main scientometric criteria, i.e., the year, number, and type of the publications, the contributing countries, the keywords, the authors, the cited authors, the cited journals, the categories in which they have been published, and the most cited documents. Consequently, the trends and the milestones in the application of the biochar as a soil amendment were marked, and therefore, based on the obtained results, a comprehensive discussion was developed, which are provided in the first chapter of this thesis. Moreover, this study has been further converted in an article which has been recently published in the Chemical engineering journal with the corresponding title as "Scientometric analysis and scientific trends on biochar application as soil amendment"(Kamali *et al.*, 2020).

In addition, due to stringent regulations established by the authorities such as the European Union and lack of available land (Kamali and Khodaparast, 2015), the troublesome sludges achieved from the treatment of different types of the wastewater are not allowed to be landfilled any longer. As a result, this waste has become a resource and as mentioned above, the sludges of different types of wastewaters are gaining attention to be utilized as the feedstock of biochar production. The conversion of the sludge into biochar can be accounted as a novel mean of waste management (Sadeghi *et al.*, 2018) and it can promote a crucial role towards obtaining the circular economy in the wastewater treatment process (Bolognesi *et al.*, 2019). Moreover, the application of the sludge-derived biochar can be accounted to be in compliance with the sustainable development goals 2030 assigned by the United Nations (Shackley *et al.*, 2011) (United Nations, 2016). The main goals that can be targeted and obtained via the application of such a biochar can be as the following;

- Sustainable Development Goal number 15: "life on land": due to the fact that the application of the biochar can promote the means to reduce the soil degradation as it can enhance the physical and chemical properties of the soil such (Liu *et al.*, 2018);
- Sustainable Development Goal number 2: "zero hunger": due to the fact that the application of the biochar promotes the improvement of the physical and chemical properties of the soil, the enhancement in the crop yield from the agricultural

activities can be achieved which can aid the combat of the food provision and can considerably contribute to obtain zero hunger for all the people all around the world (Mehmood *et al.*, 2017);

- Sustainable Development Goal number 13: "climate action": the application of the biochar can provide a source of C in the soil which can be accounted as a C sequester in the soil. Moreover, due to the fact that it can be utilized as a fertilizer, its application can contribute to the reduction in the GHGs release into the atmosphere as a result of the agricultural activities. Thus, with these two features, it can be concluded that the application of the biochar can be considered as means towards climate change mitigation (Hansson *et al.*, 2020);
- Sustainable Development Goal number 7: "affordable and clean energy": in the process of the biochar production, other products as bio-oil and py-gas, which can be utilized as a source of energy (specifically the liquid by-product) and the promotion of the clean energy sources can be obtained (Bolognesi *et al.*, 2019).

Thus, it can be stated that the application of the biochar as a soil amendment complies with the definition of the "sustainable development" stated in the "Brundtland Report", aka "Our Common Future" as the present needs can be met while the needs of the future generation will not be undermined (World Commission on Environment and Development, 1987).

As the characteristics of the biochar mainly is determined based on the properties of the utilized feedstock, the behaviour, the consequences, and the destiny of the application of the sludge-derived biochar remain uncertain and careful analysis is required for a safe and commercial application of the biochar produced from the sludges.

Thus, an experimental study was performed on the application of biochar produced from the secondary sludge of the pulp and paper mill of Portugal. To proceed with this experiment, primarily, the biochar was produced under certain pyrolysis condition of 450°C as the highest temperature, the rate of 10°C/min, and the residence time of 2 hours. Further on, the produced biochar was analysed regarding its physical and chemical characteristics. Thereafter, the produced biochar was applied in forest soils of the industry and it was supplied by them, and then, the mixtures went through the incubation and phytotoxicity tests. The obtained results in this regard are demonstrated in the second chapter of this thesis. Also, the obtained results have been presented in the "2nd International Conference on Environmental Sustainability and Climate Change" in November 2019, Rome, Italy. These experiments as the biochar production and the analysis regarding its behavior and toxicity were performed as a part of the project

"PROTEUS – Products and technologies for the sector of *Eucalyptus* globulus", with reference POCI-01-0247-FEDER-017729, through Fundo Europeu de Desenvolvimento Regional (FEDER) in the scope of COMPETE – Programa Operacional de Competitividade e Internacionalização (POCI), Portugal 2020.

Chapter 1: Scientology and Scientific Trends in the Application of Biochar as Soil Amendment

1. Introduction

Biochar is the solid product of biomass thermochemical conversion, which is conducted in the absence of O_2 at temperatures higher than 250 °C (pyrolysis), and with residence times ranging from seconds up to hours or days. Such products have basically high carbon content and high specific surface area (Joseph *et al.*, 2018; Rizwan *et al.*, 2018; Situmeang *et al.*, 2016). Hence, number of applications can be expected for such products, especially where a material with high carbon content and/or a vast adsorption is required (Chen *et al.*, 2019; Dai *et al.*, 2019; Guo *et al.*, 2019; Shaaban *et al.*, 2013). Application of biochar is also considered as a possibility to capture and storage of carbon in soil in order to mitigate adverse environmental impacts such as climate change (Aviso *et al.*, 2019). For specific applications such as soil amendment, innumerable published works stating the applications of biochar that can bring a number of advantages such as enhancement of soil fertility and improvement of soil properties for agricultural applications(Zama *et al.*, 2018). Moreover, a number of published documents in the literature have clearly emphasized the potential application of biochar as a soil amendment, in compliance with the sustainable development goals assigned by the United Nations (due to being recognized as a climate change mitigator, waste management, and waste as resource) (Keesstra *et al.*, 2018, 2016; Rodrigo-Comino *et al.*, 2018). It can be also attributed to high nutrient content of the biochar as well as its ability to absorb and immobilize toxic elements such as heavy metals, especially Cd and Cu from the soil (Bashir *et al.*, 2018; Connor *et al.*, 2018; Guemiza *et al.*, 2017; Shen *et al.*, 2018). Also, pH adjustment with biochar is considered an effective way to re-use the soils with low pHs such as those from mining activities (Shen *et al.*, 2018). Such positive effects can also result in the enhancement of microbial activity, leading to improved soil fertility (Wu *et al.*, 2019).

There are many pieces of evidence in the literature that the application of biochar, produced mainly from animal manure and fish bones, was first practiced in Ancient Amazon as far as 2500 years ago. The product of such practices is called "black earth" ("terra preta" in Portuguese) with a high carbon content. There is also some proofs of biochar application in many other regions of the word such as in Egypt, Japan, and Greek. Although the Egyptian kilns, used historically for the production of biochar, are still in use, they are energy consuming, with high rate of atmospheric emissions, and there is no potential of by-products (such as bio-oil and syngas) recovery (Laird *et al.*, 2009) to promote a clean source of energy which can also compensate for the pyrolysis process which is accounted as a highly energy consuming procedures (Bridgwater, Meier and Radlein, 1999)

The properties of the biochar and, therefore, its behaviour and effects on the amended soil, mainly is determined by the feedstock utilized for the purpose of the biochar production and also the pyrolysis condition applied (Zhang *et al.*, 2018). Nowadays, there is a market for the biochar derived from the agricultural wastes and produced from biomass (Yu *et al.*, 2017). The current market for the biochar produced from the above-mentioned feedstock, is mainly oriented in retails regarding the gardening, vineyards, landscapes, storm water, wastewater treatments, etc (Gillett, Sorrel and Ranch, 2017). However, there is no certainty regarding its price and it is defined based on its effect on the C content of the soil and also the enhancement it can cause on the crop yield of the agricultural activities applying the biochar as a soil amendment (Laird *et al.*, 2017). Also, it has been noted that the application of the biochar can indirectly contribute to the reduction of the prices of the fertilizers and increase the value of the land on which it has been utilized due to the enhancements it can cause on the properties of the soil (Laird *et al.*, 2009). However, there is also a hypothesis regarding the current market of the biochar that declares that there is not an actual market for the biochar and the place that it is used is accounted as the market (Silva *et al.*, 2019). Moreover, an encouragement has been established regarding the replacement of bulk coal with the biochar which can alter the position of the biochar in the market into a whole new level (Laird *et al.*, 2009). Nonetheless, the uncertainties regarding the biochar market, price, and other aspects of the biochar especially produced from the feedstocks as sludges and municipal wastes remain unanswered (Raheem *et al.*, 2018).

The present study on the application of biochar as a soil amendment raises the question regarding the current stage of the science and technology in this field (Zandi *et al.*, 2019). Also, this scientometric study aimed at determining the trends in the scientific community which can facilitate to mark the deficiencies and the areas with the need for urgent improvements to accelerate the commercialization of the biochar for soil application. Moreover, an analytical overview on the state of the science in this field would be highly beneficial to support the sound scientific conclusion on the scientific history, the progress made, previous and current trends in this field, identifying the gaps and potentials for further progress. The present study aims to provide a comprehensive scientometric analysis of the global efforts made on the production of biochar for soil applications based on the published pieces of the evidence in the literature. The results will support scientific community with an in-depth understanding of the status of science as well as the research trend in this field.

2. Methodology

To proceed with the scientometric study, at first, the database was selected to retrieve the related documents. Among the existing database including Google Scholar, Scopus, and ISI Web of Science (WoS) core collection, ISI WoS core collection was adopted because it contains the indexed journals, conference proceeding papers, etc., (Marsilio, Cappellaro and Cuccurullo, 2011; Olawumi and Chan, 2018; Wang *et al.*, 2016). CiteSpace (5.3.R4) with the ability to provide visualized comparisons and also the network analysis (Chen, 2017) was used for the treatment and presentation of results. It must be stated here that ISI WoS core collection outputs are compatible with the CiteSpace as input raw data (Kuo, 2008). According to pre-literature review, a combination of keywords including "TI=((biochar OR biocarbon OR pyroli* OR biomass product) AND (Soil OR fertili* OR plant OR Grow* OR Compost*)) was used in the advance search mode of ISI WoS core collection. As can be observed, this bibliographic search was combined with a fuzzy string represented as "*", which provides wider ranges of words related to "pyrolysis", "fertilize", "grow", and "compost".

In this research, English documents published in between 2000 and 2018 were collected on 11th May 2019 and the search was orientated based on the appearance of intended keywords in the titles of the documents. A critical screening on the retrieved bank was performed in order to be sure about the accuracy of the data collected. The relevant papers were selected into the "marked list" of WoS and then, they were exported from WoS in the format of "plain text" and were inserted in CiteSpace (5.3.R4) to be analyzed regarding their specific characteristics. The scientometric criteria, which were taken into consideration in this analysis are: (1) publication type, (2) publication year, (3) contributed countries, (4) keyword, (5) author, (6) cited authors, (7) cited journals, (8) categories, and (9) cited documents. The parameters applied to perform scientometric analysis of the biochar application for soil amendment include:

a) Betweenness centrality (BC)

This parameter represents specific characteristics of any node located in a network (R, Balakrishnan and Jathavedan, 2014). BC, which accounts to assess the links between nodes (e.g., authors), measures the possibility of fitting any node in the shortest path between two other nodes. Its relevant value varies between zero and one (Freeman, 1977).

b) Citation burst (CB)

The concept of "burst" refers to a frequency of a topic growing acutely as the topic appears and eventually, fades after a duration. Citation burst is a tool to measure the enhancement in the citations received by either a specific author or a document over a certain period of time (Kleinberg, 2003).

c) Sigma

Sigma is a pre-defined parameter in CiteSpace accounted as an integrated measurement of the strength and the characteristics of the nodes including BC and CB, respectively (Chen, 2017).

d) Citation counts (CC)

Citation counts criterion deals with the number of times that a specific document, author, or journal has been citated since its publication date over a certain period of time known as an exposure time. CC includes all the citations received including self-citations. The number of co-authors of any specific document can potentially affect the CC (Chen, 2012).

e) Citation frequency (CF)

Citation frequency is calculated by the division of CC of any publication by its considered exposure time (United States Environmental Protection Agency, 2004).

f) Clustering

Clustering is a technique employed by CiteSpace that classifies the input data such as keywords and authors of the publications into sub-categories. The strongest cluster, represented as "#0", stands for a category containing elements with the highest level of similarity to one another (Cornish, 2007; Olawumi and Chan, 2018).

3. Results

By applying an advance search in WoS database using the mentioned set of keywords (section 2), a total of 2123 English documents were collected for the considered period (2000 till late 2018). In the following, results achieved from the execution of research design is presented according to the selected scientometric parameters mentioned in Methodology section.

3.1 Publication type analysis

Among the bibliographic documents gathered, research articles shared the highest portion with 86% of all the publications over the studied period of time. Figure 1.1 represents the respective results obtained.

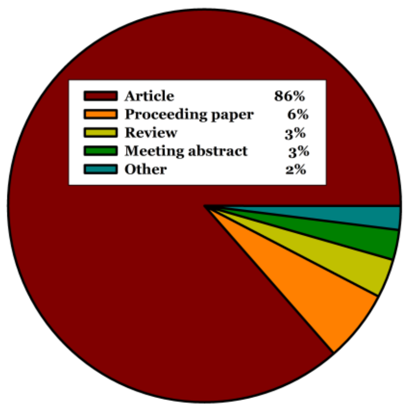

Figure1. 1 Types of documents published on the application of biochar for soil amendment.

3.2 Distribution of publications over the years

Distribution of various types of publications over the studied period of time can give an overview on the progress made in this field. In this regard, the total number of published documents on the application of biochar for soil amendment over the adapted duration, extracted from WoS, was precisely analyzed. The obtained results (Figure 1.2 and Table 1.1) revealed that a publication in this field was initiated since the 2000s. However, until 2008, the number of bibliographic documents did not show a noteworthy growth. Afterwards, rapid growth was observed, especially after 2010. The cumulative number of published documents also demonstrate sigmoidal pattern (R2=0.99) as illustrated in Figure 1.2b. It may be noticed that the number of publications in this scientific area has reached a certain point of maturity.

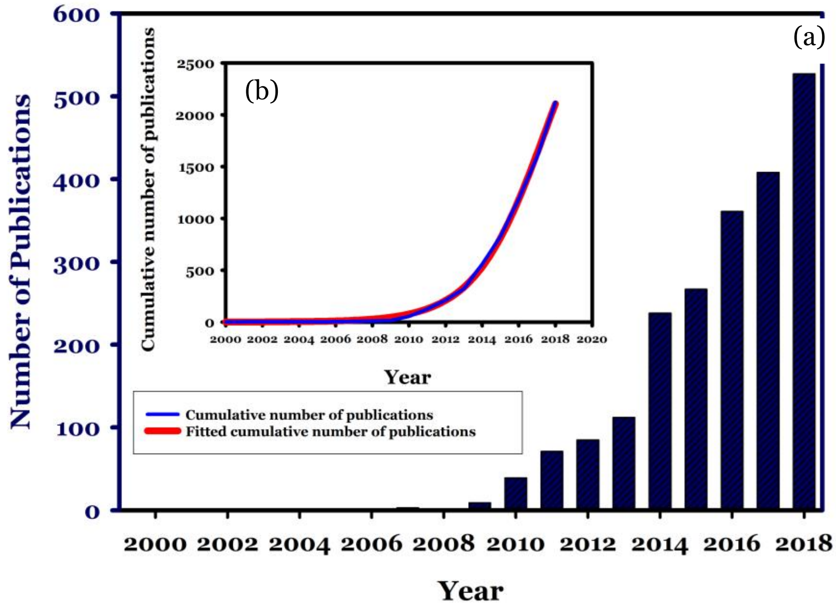

Figure1. 2 The number of published documents on the application of biochar for soil amendment (a) and the cumulative number of publications indicating sigmoidal pattern of growth with and without curve fitting (b).

Table 1. 1 Distribution of publications indexed in WoS on the application of biochar for soil amendment.

Number	Year	Publication (No.)	Contribution (%)
1	2018	527	24.82
2	2017	408	19.22
3	2016	361	17.00
4	2015	267	12.58
5	2014	238	11.21
6	2013	112	5.28
7	2012	85	4.00
8	2011	71	3.34
9	2010	39	1.84
10	2009	9	0.42
11	2007	3	0.14
12	2006	1	0.05
13	2004	1	0.05
14	2000	1	0.05

3.3 Contributing countries analysis

The most contributing countries in the publication of scientific documents in this field were recognized from the analysis provided by WoS database. As can be realized from Figure 1.3 and Table 1.2, China (with 763 documents) is the most contributing country. The USA and Australia with considerable differences to China occupied the next places among the leading countries with 404 and 217 documents, respectively published in the literature. Also, there is no notable difference among the three upcoming countries including Germany (147 documents), Spain (132 documents), and South Korea (114 documents) in terms of their publications on biochar application to improve soil physicochemical properties.

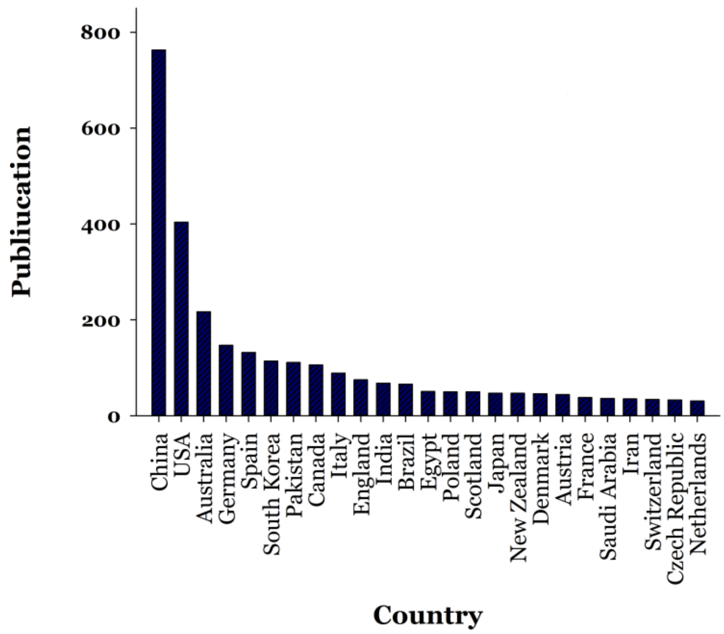

Figure1. 3 Contribution of various countries worldwide in the production of scientific documents on the application of biochar for amendment of soils.

Table 1. 2 Contributing countries in the publications on the application of biochar for soil amendment.

Rating	Country	Count (No.)	Contribution (%)
1	China	763	35.94
2	USA	404	19.03
3	Australia	217	10.22
4	Germany	147	6.92
5	Spain	132	6.22
6	South Korea	114	5.37
7	Pakistan	111	5.23
8	Canada	106	4.99
9	Italy	89	4.19
10	England	75	3.53

3.4 Keyword analysis

Co-occurring of the collected keywords appearing in the documents were analyzed using the CiteSpace. As can be observed, keywords including “biochar”, “black carbon”, and “charcoal” have appeared most frequently (in number of 1081, 468, and 450, respectively) among all the applied keywords to represent the documents published on the application of biochar for soil treatment. "Amendment", "carbon", and "soil" are the up-coming keywords from the frequent perspective, in number of 411, 332, and 270, respectively, which can demonstrate the focus of the studies performed so far in this field. It can also be stated that keywords including "biochar" and "black carbon" have the highest centrality strengths among others. In terms of burst strength, "Charcoal" received the highest score. Figure 1. 4 and Table 1.3 show the results provided by CiteSpace with a minimized overlap.

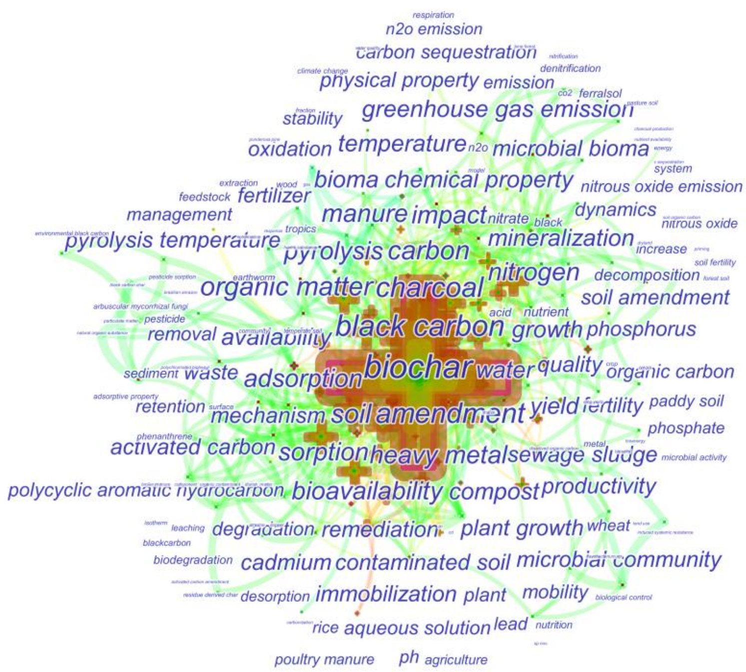

Figure1. 4 A schematic representation of co-occurring analysis of the keywords appeared in scientific documents published on the application of biochar for soil treatment. In this figure, the centrality has been neglected to represent clearer illustration. The figure containing the exact centrality is provided in the supplementary information.

Figure 1. 5 is designed to demonstrate the trends in the evolution of keywords introduced by the authors to represent their scientific publications on the production and application of biochar for soil amendment activities.

Table 1. 3 Output of keywords co-occurring analysis, and respective parameters of scientometric analysis. These keywords are most widely used to represent scientific documents published so far on the application of biochar for soil amendment.

Rank	Keyword	Sigma	Centrality	Burst	Frequency
1	Biochar	1	0.34	-	1081
2	Black Carbon	1.89	0.1	6.88	486
3	Charcoal	3.16	0.06	19.46	450
4	Amendment	1	0.13	-	411
5	Carbon	1	0.05	-	332
6	Soil	1	0.06	-	270
7	Organic Matter	1	0.02	-	250
8	Sorption	1	0.1	-	237
9	Heavy Metal	1	0.08	-	234
10	Pyrolysis	1.05	0.03	2.03	234
11	Bioavailability	1	0.09	-	228
12	Nitrogen	1	0.08	-	222
13	Impact	1	0.03	-	212
14	Adsorption	1.15	0.1	1.39	209
15	Manure	1.07	0.05	1.28	193
16	Water	1	0.01	-	154
17	Chemical Property	1	0.05	-	153
18	BioMa	1.01	0.01	2.29	152
19	Growth	1	0.02	-	150
20	Availability	1	0.09	-	135
21	Yield	1.01	0.02	0.37	129
22	Compost	1.04	0.07	0.49	128
23	Greenhouse Gas Emission	1	0.04	-	128
24	Temperature	1	0.02	-	128
25	Mineralization	1	0.06	-	128

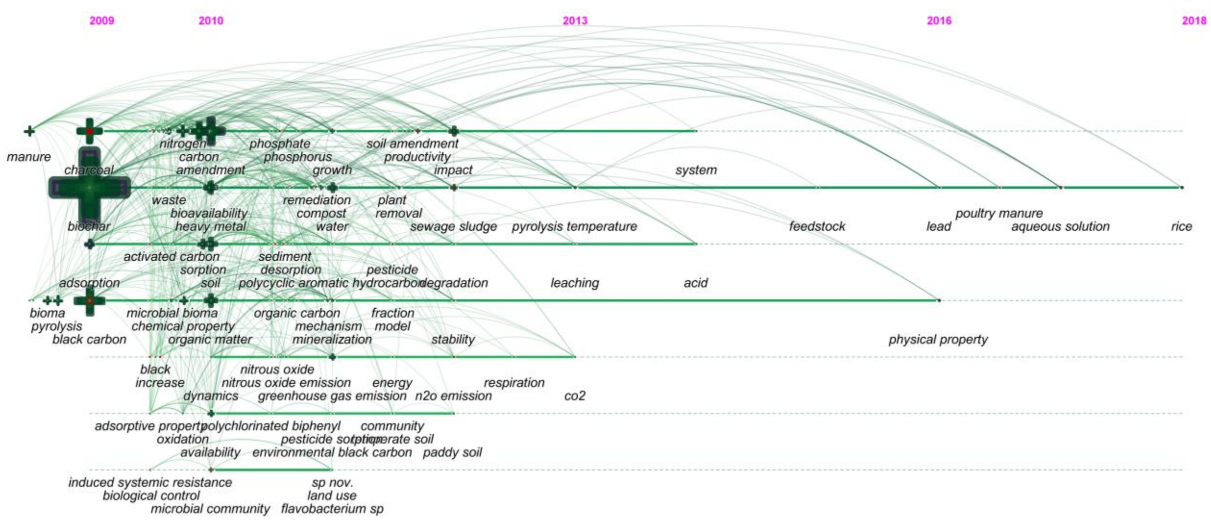

Figure1. 5 Appearance of timeline of keywords applied to represent the scientific documents published on the application of biochar for amendment of soil.

From Figure 1. 5, it is observed that most frequent keywords, “biochar”, “black carbon”, and “charcoal”, have appeared simultaneously in 2009. Hence, this year is considered as the main milestone in the scientific knowledge in this field. Also, it can be concluded that most of the keywords have been applied for the first time before 2013 and only a limited number of them have appeared after this date.

3.5 Author analysis

“Authors” represent the contribution of authors of scientific publications on biochar application for soil treatment and results of this analysis are provided in Figure 1. 6 and in Table 1. 4. The nodes stand for contributing authors in this field, while the links represnt their cooperations. Also, the fonts representing the names of authors are to visualize their extent of contributions. The bigger the utilized font, the more contribution author had. As can be observed in Figure 1. 6, “Yong sik Ok”, shown as OK YS, with 68 documents from South Korea, “Van Zwieten” with 31 documents from Australia, and “Pang GX” with 27 documents from China contributed as the leading authors in the field. Of these, Yong sik Ok is currently recognized as the most active author who has worked on various diciplines of the biochar preparation with enhanced properties (Wu *et al.*, 2019) from various sources (Shaheen *et al.*, 2019) for different applications such as adsorption of hazardous materials from air (Khan *et al.*, 2019), soil (Wu *et al.*, 2019), and aqueous media (Aftab *et al.*, 2019; Shaheen *et al.*, 2019), and on agricultural applications (Palansooriya *et al.*, 2019), etc. However, the present work is restricted to only soil applications.

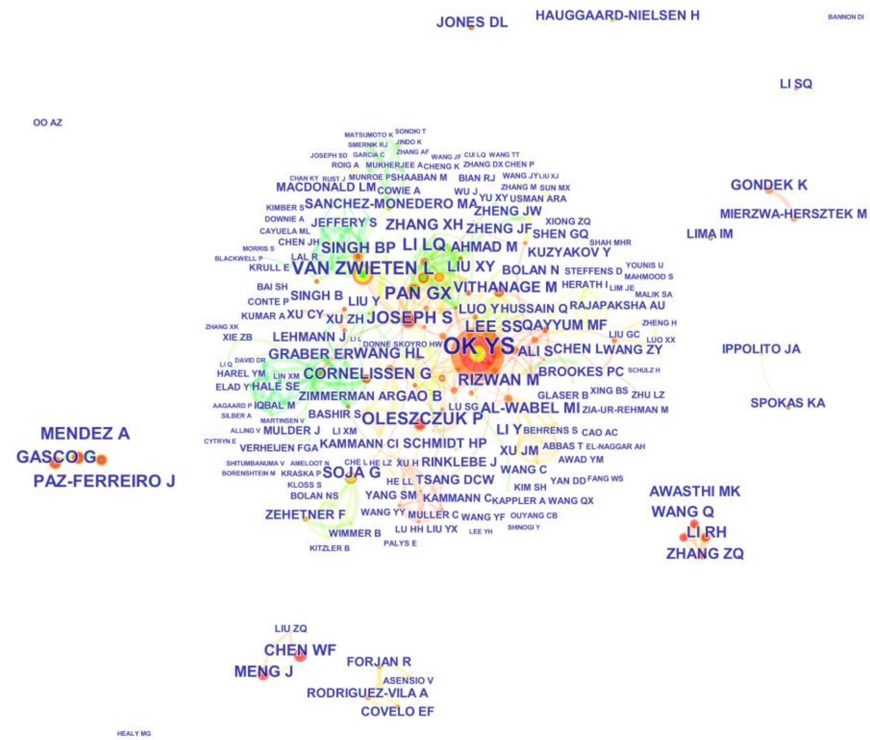

Figure1. 6 A schematic to illustrate the authors contributed in scientific publications on the application of biochar for soil amendment. This figure is produced with minimum overlaps. The figure containing the exact centrality is provided in the supplementary in supplementary information. This analysis was performed considering all the authorship team members.

Table 1. 4 The list of contributing authors in the application of biochar for soil amendment including the detailed information and their respective countries.

Rating	Author	Country	Count (No.)	Contribution (%)
1	OK YS	South Korea	68	3.20
2	Van Zwieten L	Australia	31	1.46
3	Pan Gx	China	27	1.27
4	Joseph S	China	25	1.18
5	Gasco G	Spain	24	1.13
6	Li LQ	China	24	1.13
7	Mendez A	Australia	24	1.13
8	Paz-Ferreiro J	Norway	22	1.04
9	Cornelissen G	Norway	21	0.99
10	Meng J	China	21	0.99
11	Chen WF	China	20	0.94
12	Lee SS	South Korea	20	0.94
13	Oleszczuk P	Poland	20	0.94
14	Singh BP	Australia	20	0.94
15	Zhang ZH	China	20	0.94
16	Rizwan M	Pakistan	19	0.90
17	Vithanage M	Sri Lanka	19	0.90
18	Wang HL	China	19	0.90
19	AL-Wabel MI	Saudi Arabia	18	0.85
20	Graber ER	Israel	18	0.85

3.6 Cited authors analysis

"Cited authors" analysis was performed by utilization of the scientometric parameters introduced in the methodology section including CC, CB, centrality, sigma, and clustering. Regarding the CC analysis, Lehmann J (cluster#3), Glaser B (cluster#1), and Spokas KA (cluster#0) with the frequencies of 1398, 579, and 545, respectively are considered as the highlighted authors. With regard to CB analysis, Ahmad M (2015, cluster #6), Yanai Y (2010, cluster#0), and Wang J (2017, cluster#0) have the highest burst strengths of 26.83, 26.74, and 25.61, respectively. For the centrality, Lehmann J (cluster#3), Major J (cluster#1), and Zimmerman AR (cluster#0) have the highest respective centralities of 0.45, 0.16, and 0.13 among all the authors published in this field. With regard to sigma analysis, Schmidt (cluster#3), Ahmad M (cluster#6), and Yu XY (cluster#3) have the highest sigma of 4.48, 3.64, and 3.62, respectively among others. Figure 1.7 and Table 1. 5 show the respective data as an output of CiteSpace. It is also worthy to mention that "Yong sik Ok" is identified as a highly cited authors for the aplication of biochar for various applications (Abbas *et al.*, 2017; Ahmad *et al.*, 2012, 2014; Beiyuan *et al.*, 2017; Igalavithana *et al.*, 2017; Inyang *et al.*, 2016; Lee *et al.*, 2017; Mohan *et al.*, 2014; Niazi *et al.*, 2018, 2018; Park *et al.*, 2016; Poucke, Van *et al.*, 2018; Rajapaksha *et al.*, 2015, 2016, 2018). As well, he has published hot (El-Naggar *et al.*, 2018) and highly cited papers (Ahmad *et al.*, 2017; Alam *et al.*, 2018; Ali *et al.*, 2017; Beiyuan *et al.*, 2017; El-Naggar *et al.*, 2018, 2019; Hussain *et al.*, 2017; Shen *et al.*, 2018) for the application of biochar for soil amendment purposes.

In addition, the analysis of clustering, with the top seven clusters according to their size, of the cited authors is shown in Figure 1. 8. This clustering analysis has been implemented over the obtained cited author analysis demonstrating the main focus of research of the most cited authors. The first three largest clusters of keywords represented are as follows. The cluster#0, entitled as "potential mechanism", with cluster strength of 1.6 was formed in 2012, and contains 28 members. The most active citer in this cluster is "XU, G" (2012, for the document entitled "Recent advances in biochar application in agricultural soils: benefits and environmental implications" published in the journal of "Clean – Soil Air Water") (Xu *et al.*, 2012). The cluster#1, entitled as "nutrient status", has the cluster strength of 0.77 and was arranged in 2011, containing 25 members. The cluster#2 with the similar title to the cluster#0, with the cluster strength of 0.68 has 20 members. It can also be stated that the potential mechanisms involved in the application of biochar as a soil amendment has gained the most attention by the authors and other aspects such as nutrient status (cluster#1), (biochar to soil) molar ratio (clusters#3 and 4), and soil (properties) (cluster#5) were received the next importance by the most cited authors. The similarity in the title of these two clusters represents the fact that the potential mechanism involved in the biochar application is currently a hot topic in the literature (Boqiang and Tong, 2020). This point should also be emphasized that the clustering analysis (Figure 1. 8) has been performed on the cited author scheme using centrality criterion, presented in the supplementary information. As it can also be observed from Figure 1. 8, the largest clusters (represented as cluster#0, and cluster#1), are located in the semi-center of the graph illustrating their high significances. In addition, the most active citer in both cluster#1 and 2 is “Atkinson, CJ” (2010, for the document entitled “Potential mechanisms for achieving agricultural benefits from biochar application to temperate soils: a review” published in the journal of “Plant and Soil”)(Atkinson, Fitzgerald and Hipps, 2010).

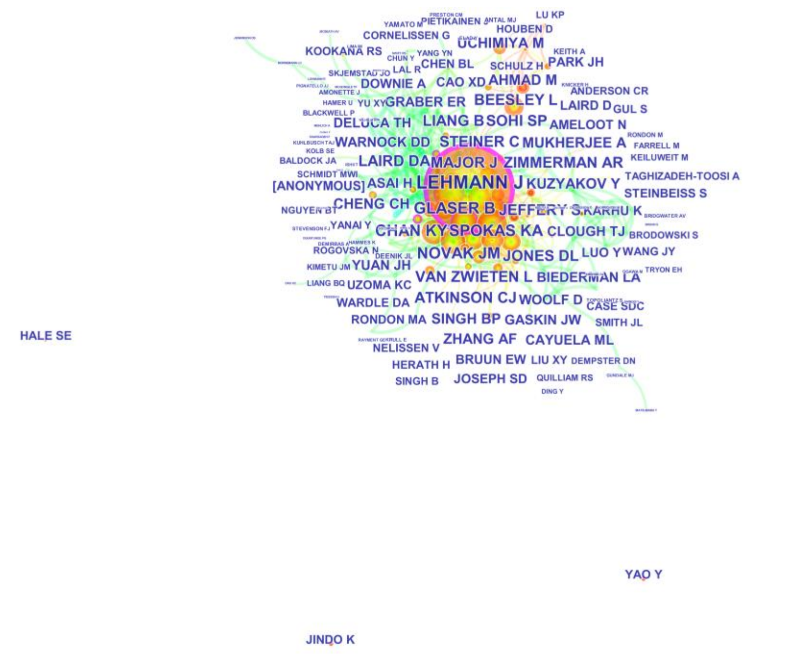

Figure1. 7 A schematic illustration demonstrating the most cited authors publishing scientific documents on biochar application for soil amendment. Graph is with the minimized overlaps. The figure containing the exact centrality has been provided in supplementary information.

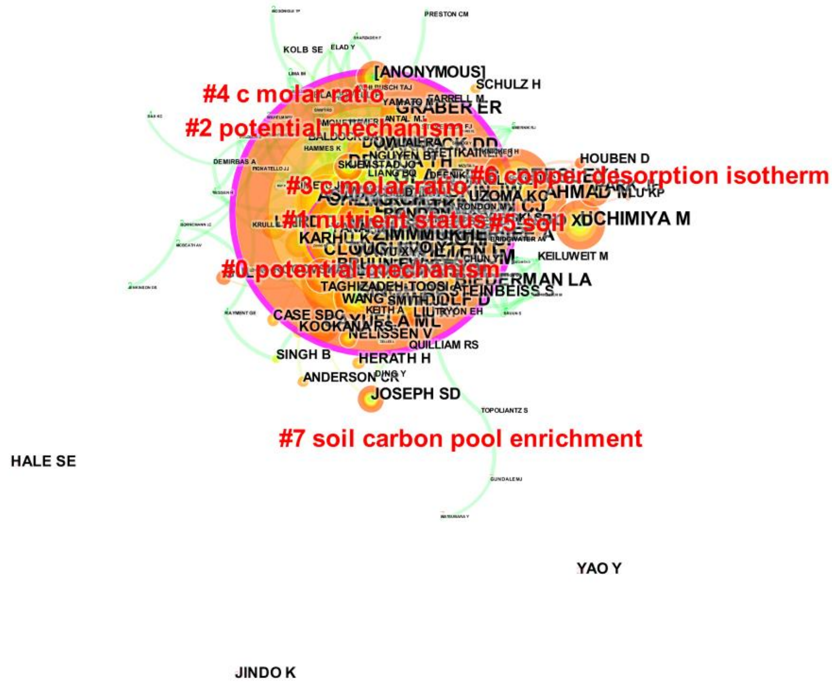

Figure1. 8 Clustering of cited authors on the application of biochar for the treatment of soils extracted using CiteSpace software.

Table 1. 5 List of the most cited authors on the application of biochar for the treatment of soils and respective parameters of scientometric analysis. The parameter "year" in this table indicates the specific year in which the citation burst was initiated.

Rating	Author	Year	Sigma	Centrality	Burst	Frequency
1	Lehmannn J	2007	2.16	0.45	2.05	1398
2	Glaser B	2007	1.34	0.11	2.88	579
3	Spokas KA	2010	1	0.04	-	545
4	Chan KY	2010	1	0.04	-	485
5	Novak JM	2010	1	0.03	-	485
6	van Zwieten L	2010	1	0.06	-	473
7	Major J	2010	1	0.16	-	452
8	Steiner C	2009	1.06	0.04	1.49	444
9	Jeffery S	2013	1	0.02	-	407
10	Liang B	2010	1.03	0.04	0.92	389
11	Laird DA	2010	1	0.07	-	385
12	Jones DL	2012	1	0.04	-	380
13	Beesley L	2011	1	0.03	-	375
14	Zimmerman AR	2011	1	0.13	-	374
15	Sohi SP	2011	1	0.02	-	354
16	Atkinson CJ	2011	1	0.01	-	345
17	Cheng CH	2010	1.06	0.02	3.03	331
18	Uchimiya M	2011	1	0	-	285
19	Kuzyakov Y	2010	1	0.05	-	281
20	Singh BP	2010	1	0.07	-	269
21	Zhang AF	2012	1.02	0.01	1.57	265
22	Mukherjee A	2014	1	0	-	257
23	Ahmad M	2015	3.64	0.05	26.83	245
24	Clough TJ	2011	1	0.01	-	242
25	Woolf D	2011	1	0	-	232

3.7 Cited journals analysis

In this section, variables regarding the number of citations related to each journal publishing the documents analysed in this study were analysed using CiteSpace software, and the results obtained are shown in Figure 1. 9 and Table 1. 6. Regarding the CC analysis, "Plant and Soil" (cluser#0), "Soil Biology and Biochemistry" (cluster#0), and "Chemosphere" (cluster#1) have shown frequencies of 1461, 1372, and 1239, respectively. The CB analysis indicated that "Geochimica et Cosmochimica Acta" (cluster#0), "Frontiers in Ecology and the Environment" (cluster#4), and "Global Biogeochemical Cycles" (cluster#3) had the burst strengths of 53.05, 50.56, and 41.26, respectively. Top journals containing the highest centralities were also identified as "Soil Biology and Biochemistry" (cluster#0, centrality= 0.13), "Biology and Fertility of Soils" (cluster#2, centrality= 0.12), and "Chemosphere" (cluster#1, centrality= 0.09). In regards with the sigma analysis, "Frontiers in Ecology and the Environment" (cluster#4), "Global Biogeochemical Cycles" (cluster#3), and "Energy and Fuels" (cluster#3) had the sigma values equal to 8.38, 4.65, and 3.23, respectively.

Moreover, the cited journal clustering analysis is shown Figure 1. 10, and the two largest clusters are as follows. Similarly, this analysis was performed on the obtained results of the most cited journal with centrality. The first cluster, represented as cluster#0 and entitled as "biochar effect", contains 22 members and the mean year of this cluster is 2009. The most active citer in this cluster is "Atkinson, CJ" (2010, for the document entitled "Potential mechanisms for achieving agricultural benefits from biochar application to temperate soils: a review" published in the journal of "Plant and Soil")(Atkinson, Fitzgerald and Hipps, 2010). The second cluster labeled as cluster#1, entitled also as "biochar effect", owns 16 members and the mean year of this cluster is 2010. The most active citer in this cluster is "Ding, Y" (2010, for the document entitled "Evolution of biochar effects on nitrogen retention and leaching in multi-layered soil columns" published in the journal of "Water, Air, and Soil Pollution") (Ding *et al.*, 2010). In this regard, it can be stated that the main focus of the relevant journals has been on the biochar effects (Boqiang and Tong, 2020). Two more smaller-size clusters (as cluster#3 entitled as "molar ratio" and cluster#4 as "biochar amendment") can also be observed in Figure 1. 10. However, the effect of biochar application and, similar to the clustering of cited authors, the potential mechanisms of biochar as a soil amendment have received the highest amount of attention in the literature. In addition, the location of cluster#2, (potential mechanism) at the center of Figure 1. 10 represents its high degree of importance, as one of the main items that the journals in this field have paid attention to that. Finally, the results of the clustering of the most cited journals is in compliance with those obtained from the most cited authors which are active in the field of biochar application as a soil amendment.

Figure1. 9 The cited journals analysis with minimum overlap obtained from CiteSpace. The analysis is based on the number of citations these journals received by publishing the documents gathered and analyzed in this study on the application of biochar for soil treatment. It is also worthy to mention that the centrality factor has been neglected when drawing this figure for a higher-quality illustration. The figure with actual centrality can be found in supplementary information.

Table 1. 6 The detailed information about the journals, which has received the citations by publishing the documents collected for the present scientometric study on the application of biochar for soil amendment, and respective parameters of scientometric analysis.

Rating	Journal	Centrality	Frequency
1	Plant and Soil	0.07	1461
2	Soil Biology and Biochemistry	0.13	1372
3	Chemosphere	0.09	1239
4	Environmental Science and Technology	0.09	1164
5	Geoderma	0.08	1058
6	Soil Science Society of America Journal	0.04	1048
7	Environmental Quality	0.05	1040
8	Biology and Fertility of Soils	0.12	1022
9	Agriculture, Ecosystems & Environment	0.03	999
10	Bioresource Technology	0.06	961
11	Australian Journal of Soil Research	0.04	927
12	Science of the Total Environment	0.03	916
13	Biochar Env Manageme	0.01	915
14	Environmental Pollution	0.04	716
15	European Journal of Soil Science	0.01	696

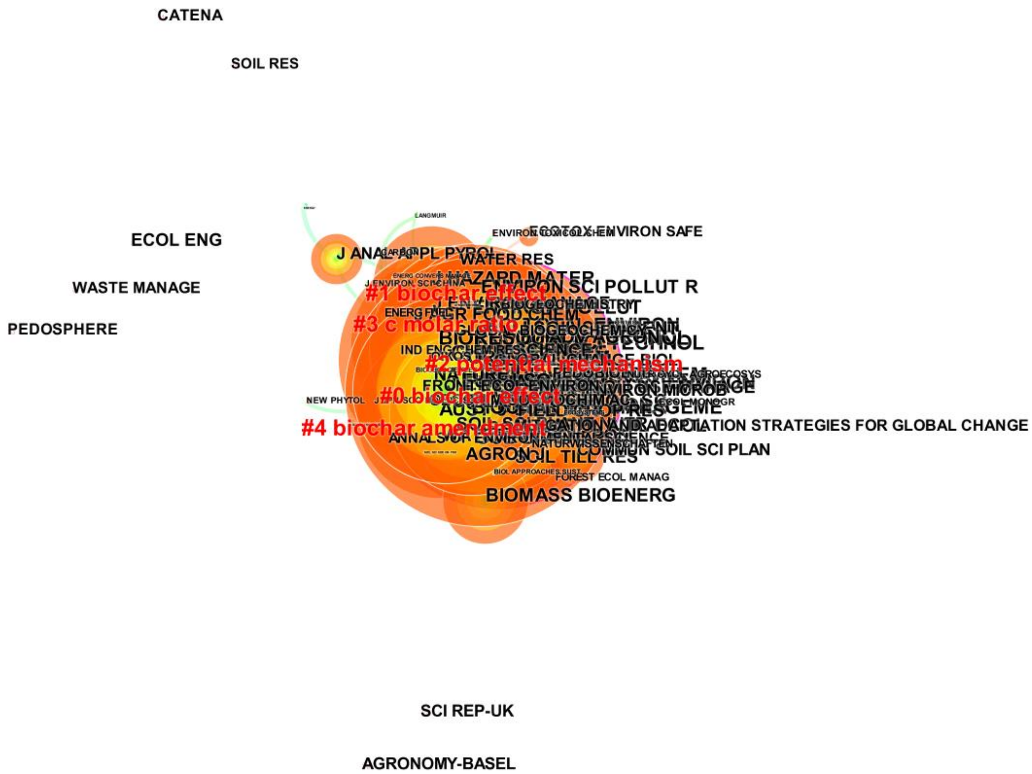

Figure 1. 1 A schematic of the most cited journals clustering process, obtained from CiteSpace. The citations have been counted only for the documents gathered for the present scientometric study.

3.8 Categories

Categories analysis classifies the scientific documents published on the application of biochar for the soil treatment in specific categories regarding their specific attributes such as representative scientific area analyzed using WoS database. Table 1. 7 shows the detailed results achieved in this regard, and the most important categories identified in this field are “Environmental Science” (891 documents), “Soil Science” (598 documents), and “Agronomy” (278 documents).

Table 1. 7 Information regarding the categories of published documents obtained from WoS.

Rank	Categories	Count (No.)	Contribution (%)
1	Environmental Science	891	25.54
2	Soil Science	598	17.14
3	Agronomy	278	7.97
4	Plant Science	163	4.67
5	Engineering Environmental	150	4.30
6	Agricultural Multidisciplinary	145	4.15
7	Energy Fuels	130	3.72
8	Ecology	109	3.12
9	Biotechnology Applied Microbiology	105	3.01
10	Water Resources	90	2.58
11	Multidisciplinary Science	75	2.15
12	Agricultural Engineering	68	1.94
13	Chemistry Multidiciplinary	64	1.83
14	Green Sustainable Science Technology	62	1.77
15	Geosciences Multidisciplinary	57	1.63
16	Chemistry Analytical	48	1.37
17	Food Science Technology	42	1.20
18	Horticulture	41	1.17
19	Engineering Chemical	40	1.14
20	Toxicology	36	1.03

3.9 Cited documents

The results obtained from WoS analysis regarding the most cited documents published in the literature on the application of biochar for soil amendment is shown in Table 1. 8. As can be observed, “Biochar effects on soil biota - A review” (Lehmann *et al.*, 2011) (2011, CC= 1335), “Dynamic Molecular Structure of Plant Biomass-Derived Black Carbon (Biochar)” (Keiluweit *et al.*, 2010) (2010, CC= 953), and “Biochar as a sorbent for contaminant management in soil and water: A review” (Ahmad *et al.*, 2014) (2014, CC=949) are the leading documents in this field.

Table 1. 8 The list of the most cited documents in this field obtained from WoS.

Rating	Title	Year	journal	Citation (No.)
1	Biochar effects on soil biota - A review	2011	Soil Biology and Biochemistry	1335
2	Dynamic Molecular Structure of Plant Biomass-Derived Black Carbon (Biochar)	2010	Environmental Science and Technology	953
3	Biochar as a sorbent for contaminant management in soil and water: A review	2014	Chemosphere	949
4	Potential mechanisms for achieving agricultural benefits from biochar application to temperate soils: a review	2010	Plant and Soil	752
5	A review of biochar and its use and function in soil	2010	Advances in Agronomy	747
6	A quantitative review of the effects of biochar application to soils on crop productivity using meta-analysis	2011	Agricultural Ecosystems & Environment	689
7	Agronomic values of green-waste biochar as a soil amendment	2007	Australian Journal of Soil Research	666
8	Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil fertility	2010	Plant and Soil	590
9	Positive and negative carbon mineralization priming effects among a variety of biochar-amended soils	2011	Soil Biology and Biochemistry	554
10	Impact of Biochar Amendment on Fertility of a Southeastern Coastal Plain Soil	2009	Soil Science	501

4. Discussion

4.1 General considerations

Biochar is a carbon-neutral or carbon-negative compound, which is generally produced by the thermal decomposition of an organic feedstock (plant whether crop or residues), animal based, sludges (municipal or industries), and solid waste (agricultural or municipal)) in the absence or limited presence of O_2 (Chandra and Bhattacharya, 2019; Joseph *et al.*, 2018). The type of feedstock fed into the pyrolyzer (kiln) and also the applied pyrolysis conditions (e.g., the highest temperature, the heating rate, and the residence time) can directly determine the properties of the biochar produced (Chandra and Bhattacharya, 2019) such as total carbon content, ash content (Sohi *et al.*, 2010), liming ability (pH) (Laird *et al.*, 2009), leaching and bioavailability of nutrients and toxic metals (Khadem and Raiesi, 2017), surface area, porosity (Penido *et al.*, 2019), etc. Various reasons have been reported in the literature for the positive effects of biochar on soil properties, especially for agricultural applications. Its role in soil decontamination has been reported by the adsorption of potential toxic metals such as Cd and Cu, which may result in the decrease of bioavailability of such potential toxic metals for the plants (Abbas *et al.*, 2018; Kamali *et al.*, 2019; Lal *et al.*, 2019). It also provides the required nutrients for plant growth because biochar is usually enriched with various chemical elements such as C, Fe, Mn, Zn, etc. (Ahmad *et al.*, 2012; Kinney *et al.*, 2012; Kloss S, Zehetner F, Dellantonio A, Hamid R, Ottner F, Liedtke V, Schwanninger M, Gerzabek MH, 2012; Mukherjee and Zimmerman, 2013). It can also contribute to the improvement of critical properties of the soil such as water holding capacity (WHC) as well as bulk density and, as mentioned above, porosity, which may result in better fertility of the soil for crop production (Li *et al.*, 2018). Moreover, there are also some pieces of evidence in the literature for the positive effects of biochar with alkaline nature on the pH of the soil, which is among the main limitations for some soils such as those, which have been under mining activities (Shen *et al.*, 2018). However, it must be stated that the number of reports on the application of biochar for large-scale and field applications (Fidel, Laird and Parkin, 2019; Jin *et al.*, 2019) is still limited in the literature. Reviewing the related literature could demonstrate some potential for improvements in the application of biochar for soil improvement. For instance, although studies performed recently revealed that biochar can significantly improve the microbial activity of the soil, there are some problems for further investigations such as specific impacts of the biochar on the functioning of microorganisms in carbon and nitrogen cycle (Li *et al.*, 2018). Also, the effect of biochar addition on the soil respiration component, including autotrophic and heterotrophic has not been understood well yet (Mitchell *et al.*, 2015). The need for additional fertilizers besides biochar is another field of interest in this regard, for which there is limited information in the literature. The cost effectiveness of the biochar application compared to other existing methods to improve the soil properties can be also considered a fertile field with the need for further efforts to distinguish the real cost-effectiveness of this method compared to the conventional approaches for soil amendment. In addition, although most of the studies carried out have reported the positive effects of the biochar on the properties of the soils, the real fate of the potential toxic metals, volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs) and other matters released from biochar have not been well understood (Dutta *et al.*, 2017). Moreover, the so called "exact biochar service life" is still poorly understood. In other words, the decomposition of biochar in soil has not been well-studied to determine the required period of amendment with biochar (Ding *et al.*, 2016). Thus, in order to determine the growth of science in the application of biochar as a soil amendment and also to distinguish the trends and milestones in this field, a scientometric study was conducted. The obtained results are discussed in separate sections as follows.

4.2 Scientific documents

According to the existing literature, it can be stated that the application of biochar for soil redemption is still in the pre-commercialized phase (Roberts *et al.*, 2015). This can be due to two main reasons including the expense of the pyrolysis process and the existing uncertainties regarding the toxic consequences which may be caused or induced by the addition of various types of produced biochars (Laird *et al.*, 2009). Moreover, most of the conducted research in this field have been implemented in laboratorial scales with very few exceptions of field experiments (Jeffery *et al.*, 2011). On the other hand, most of the existing regulations about the contamination of soil and the corresponding limits of compounds as heavy metals such as Zn, Cr, etc., are oriented based on the corresponding amounts of contaminants in fields (Resende, de *et al.*, 2018). Thus, the effectiveness and competitiveness of biochar application for real applications still remains a question without a certain answer yet.

The results provided in this scientometric study demonstrate that most of the scientific efforts that have resulted in the indexed publications have been mainly after the 2000s. Between 2000 and 2010, only a limited number of publications have been reported in the literature regarding the application of biochar to soil, indicating that the scientific knowledge in this area was just beginning. After 2010 however, there has been a substantial increase in the number of published documents on the application of biochar with multiple behavior such as an adsorbent, a soil amendment material or a material to be used for carbon storage, and hence, for climate change mitigation (Wang *et al.*, 2018). Although the number of publications in the literature shows a growing trend, the cumulative number of documents published in the literature (Figure 1.2) indicate sigmoidal pattern. Thus, it can be concluded that research and science in this field have almost reached a degree of maturity.

Analysis of the most cited documents published on the application of biochar as a soil amendment can also reveal an emphasis on some specific features of biochar such as liming effect, high carbon content, high specific surface area, porosity, the potential to enhance the water holding capacity, cation exchange capacity, electrical conductivity, inertia and stability, the potential to immobilization of contaminants, enhancing the bioavailability of nutrients as N and P, and consequently the positive effects of biochar on the soil fertility and crop production. However, in some cases, opposite results were obtained from the experiments on the applicability of biochar for soil treatment. It can be explained by the various set-ups and experimental conditions (such as the type of soil utilized, the properties of biochar applied, the biochar to soil ratio, duration of experiments, etc.)(Ahmad *et al.*, 2014; Atkinson, Fitzgerald and Hipps, 2010; Jeffery *et al.*, 2011; Keiluweit *et al.*, 2010; Lehmann *et al.*, 2011; Sohi *et al.*, 2010).

4.3 Trends in the biochar application for soil treatment

The evolution occurred in in the science of the biochar application for soil treatment can be discussed based on the results of the scientific keywords appearance in the literature, demonstrated in Figures 1. 4 and 1. 5). In the period in which this study covers (since 2000) keywords such as “biochar”, “amendment”, “microbial communities”, “heavy metals”, “sorption”, etc. appeared in the literature in the certain milestones which can be used to identify the trends in this scientific field. From the keyword timeline, presented in Figure 1. 4, it can be observed that before 2009 and prior to introduction of the keywords such as “biochar” (as the main trend illustrated with the biggest cross) and “charcoal”, the only repeated keyword was “manure”. This is in compliance with the historical background of biochar application which can go back to 500 to 2500 years ago, which is assumed to be practiced by Ancient Amazonians, Japanese, African, Roman, and Egyptians, who used to convert the animal manure and fish bones to biochar to be applied as an amendment (Laird *et al.*, 2009). . Other relevant aspects such as the type of feedstock used and kilns, were introduced in the literature only after 2009 (Figure 1. 5). In addition some other keywords such as “nitrous oxide” and “stability”, appeared in this figure, between 2010 to 2013, can be related to the discovering of the biochar capability to eliminate the nitrogen leaching in the soil and also to release the greenhouse gases into atmosphere. Moreover, compared with the common fertilizers and liming agents employed in agriculture, biochar has demonstrated a more stable composition and remains semi-permanent while the mentioned fertilizers will vanish in a relatively short time, and contribute to release of high amounts of greenhouse gases. Also, as the agricultural activities are responsible for the release of approximate 25% of total anthropogenic greenhouse gases (mainly CO_2, then CH_4 and N_2O), the application of biochar aside from the carbon storage in soils can be considered as a tool to mitigate the climate change (Semida *et al.*, 2019).

4.4 Scientific contributions

As indicated in Table 1.3, among the contributing countries, China has the highest share in the number of publications in this field. The main reason for this high contribution may be the scientific programs followed by China, especially over the recent years. To highlight the mentioned programs, it should be mentioned that China has established two main activities including “special economic zones of the People's Republic of China”(Crane *et al.*, 2018) and “economic and technological development zones” (Zhao *et al.*, 2008) with the goal of accelerating the high-tech scientific-based activities by attracting foreign investments to facilitate the progress in this area. As a result, China, in recent years, has become the main contributor to research and development (R&D) activities, making this country a large producer of scientific articles besides the United States (Xie, Zhang and Lai, 2014).

The effective collaboration of the active authors in this field may overcome the present barriers for the wider application of biochar as a soil amendment and facilitates the eliminations of uncertainties regarding the behavior of various types of biochar prepared from various feedstock and under different pyrolysis conditions) considering the specifications of the studied soil. The results of the contributing authors analysis (Figure 1. 6), can reinforce the idea that proper scientific communications have been stablished all over the word, which would facilitate the share of the information among the scientific communities. However, among the most impacting authors in the field, there are some groups with high scientific outputs, but low degree of co-operations with other scientific communities.

The keyword clustering methodology applied on the obtained results from the cited authors analysis, can also demonstrate the main trends and frontiers of the studied field. The obtained results in this regard can emphasize that the initial and main trend in the biochar as an amending tool for soil has been the potential mechanisms of biochar interaction with the soil, expressed as cluster#0 which is the largest cluster among others. Moreover, due to the fact that the second largest cluster, expressed as cluster#1, is entitled as “nutrient status”, it can be concluded that the main variation in defining the biochar characteristics were oriented on the utilized feedstock and its corresponding properties. However, the pyrolysis condition as another main factor in determination of the biochar characteristics have not gotten the same attention and more studies in this field are required to further remove the existing barriers for the rapid commercialization of biochar as an effective soil amendment.

Cited journal analysis is also considered other important parameters to demonstrate the contributing parties in the science and technology of biochar application for soil application purposes. Based on the results obtained from the cited journal analysis, it can be concluded that the main active journals, which have received the highest number of citations, are mainly concerned about the application of biochar on the crop yield and its impacts on the microbial communities and activities in the soils. This might be due to the biochar capabilities to replace the conventional organic and inorganic fertilizers with a positive effect on the climate change.

Finally, analysing the results achieved from the categories analysis can reveal that "environment" and "agriculture" are the main categories that have attracted the attention of the contributors in the field. This can clearly reflect the potential contribution of biochar towards a sustainable waste management by satisfying the stringent environmental regulations (regarding the elimination of solid waste landfilling and conversion of a problematic substance into a chemically stable product) along with its potential for decontamination of the polluted soils, mitigation of climate change and the possible increase in the crop yield of the agricultural products. From these attractive aspects, it can be concluded that the application of biochar as a soil amendment can be in compliance with the sustainable development goals, assigned by the United Nations (Keesstra *et al.*, 2018, 2016; Rodrigo-Comino *et al.*, 2018), although more studies are required to deal with the existing uncertainties of some aspects of biochar application such as long-term effects of the biochar in the soil, as well as the most suitable feedstock, biochar production conditions and the optimum conditions for soil applications of biochar.

5. Conclusion

Biochar, a main product from biomass pyrolysis, has been utilized as an environmentally friendly amendment and fertilizer applied to a variety of soils. Its use has been referred as modifying the physicochemical properties of soils. Also, it has been accounted to be able to immobilize contaminants in the soil, sequester carbon, mitigate greenhouse gas emission, and improve the quality of the soil. Due to the fact that the application of the biochar as the soil remediation has been emerging in recent years, a scientometric analysis has been performed to map research efforts in this exciting field. To proceed with the analysis, ISI Web of Science core collection was adopted as the database and relevant bibliographic records were collected. A total of 2123 documents in English were collected within the period of 2000 to 2018. The results indicated that the subject has reached a relative maturity although there are still some barriers to overcome to promote the application of biochar for amendment of the soils for various purposes, mainly for crop production.

Chapter 2: Biochar Application in Soils: Behavior and Toxicity

1. Introduction

1.1. Biochar

Biochar (aka charcoal (Laghari *et al.*, 2016), black carbon (Keiluweit *et al.*, 2010), and pyrolysis product (Christel *et al.*, 2016)) is a product that is obtained from heating (to minimum 250°C(Zhou *et al.*, 2017) and maximum 750°C(Zama *et al.*, 2018)) an organic feedstock without or with limited presence of O_2 (pyrolysis) (Bridgwater, Meier and Radlein, 1999). The biochar is rich in organic matters, especially in C (Keiluweit *et al.*, 2010). The biochar can be applied as an amendment to various types of soils and also as a mitigator of climate change (Mohawesh *et al.*, 2018). This is due to its ability of sequestrating C. It can be the main source of C in soil when applied. Carbon is required for soil fertility and plant growth (Bass *et al.*, 2016). Thus, it can be utilized as a fertilizer and can reduce the amount of fertilizer, whether organic or inorganic, required for cultivating purposes. The reduction in the application of fertilizers in agriculture, for instance as the agricultural lime, will contribute to a decrease in the release of greenhouse gases (GHGs) (mainly CO_2 and secondly CH_4 and N_2O, etc.). As stated by Semida et al., 2019 (Semida *et al.*, 2019), the agriculture is responsible for the release of approximately 25% of total anthropogenic GHGs in 2014 with the potential of a rapid increase in this amount, due to the need for more food to feed the growing population. With the reduction in the application of fertilizers, the amount of GHGs produced from agricultural activities will be consequently decreased and mitigation in climate change can be pursued. Another interesting feature of the application of biochar as a soil amendment is its stability in soils. The addition of organic fertilizers such as agricultural residues and animal manures have a temporary effect on the C content of the soil. While it has been reported in many studies that the biochar can be considered as semi-permanent storage of C in soils (Laird *et al.*, 2009). However, this property does not include all types and may vary amid different biochars. The differences in properties of biochars are defined by the raw materials utilized as the fed feedstock to the pyrolyzers and the pyrolysis conditions (Chandra and Bhattacharya, 2019).

1.2. Biochar characteristics

The feedstock, which is utilized as the raw material to be converted into biochar, can be any type of biodegradable wastes and other organic materials. It can be as agricultural residue such as stovers (Laghari *et al.*, 2016), husks (Tan *et al.*, 2018), straws (Guo *et al.*, 2019), shells (Chang *et al.*, 2016), and stalks (Khadem and Raiesi, 2017) (of wheat, corn, maize, soybean, rice, peanut, sugarcane, etc.), lignocellulosic biomass (*eucalyptus* (Kaewpradit and Toomsan, 2019), *Lantana* *camara* (Berihun, Tadele and Kebede, 2017), *croton* (Bayabil *et al.*, 2015), *bamboo* (Wang *et al.*, 2018), *oak* (Bayabil *et al.*, 2015), etc.), manures (of cows (Nguyen *et al.*, 2018), cattle (Hairani, Osaki and Watanabe, 2016), swine (Alizadeh *et al.*, 2018), chickens (Cucui *et al.*, 2018), etc.), sludges (produced from treating municipal effluent (sewage) (Chandra and Bhattacharya, 2019), pulp and paper mill effluent (Paz-Ferreiro *et al.*, 2017), dairy effluent (Sadeghi *et al.*, 2018), etc.), and municipal solid wastes (Science, 2018). The utilized raw feedstock and its chemical characteristics are of high significance in the determination of the quality and the quantity (yield) of the produced biochar (Laird *et al.*, 2009). The converted materials have direct effects on the properties of the biochar, whether chemical and physical, affecting the behavior of biochar thereafter its addition to the soil. The chemical characteristics, influenced precisely via the feedstock, can be summarized as the total C content and the ash content of the biochar depending on the richness in minerals of the feedstock and consequently (Sohi *et al.*, 2010), the pH or the agricultural liming ability of the produced biochar (Laird *et al.*, 2009). Moreover, the amount of nutrients and the toxic compounds present in biochar depend highly on the feedstock as well (Molnár *et al.*, 2016). Also, the feedstock can establish the physical characteristics of produced biochar. The physical properties determined by the feedstock can be categorized such as the surface area and the pore volume of the biochar (Khadem and Raiesi, 2017). Aside from the type of the utilized raw material fed to the pyrolyzers, as mentioned earlier, the conditions implemented during the pyrolysis also determines the chemical and physical characteristics, and the toxicity of the biochar, too (Laird *et al.*, 2009).

The main pyrolysis conditions affecting the nature and the yield of biochar are contingent on i) highest implemented temperature, ii) the rate of reaching the temperature, iii) the residence time (duration) (Chandra and Bhattacharya, 2019), iv) carrier (inert) gas (Karim *et al.*, 2017), v) kiln (reactor and furnace) type, and vi) accessibility to O_2 and its present amount (Laird *et al.*, 2009). Accordingly, the physical and chemical properties, such as bioavailability of nutrients and metals, cation exchange capacity (CEC), mineral richness, pH, electrical conductivity (EC), physical structure, porosity, surface area, water holding capacity (WHC) (Penido *et al.*, 2019), C:N ratio (Ji *et al.*, 2018), etc., of the produced biochar are defined. In addition, other aspects such as the post-production conditions, i.e. the condition applied for the biochar to cool down, the age of utilized biochar, and the application condition, such as the type of soil and the dose of added biochar as an additive, also can directly govern the outcomes obtained from the application of such additive as an amendment (Laird *et al.*, 2009). However, the most considerable aspect among the pyrolysis condition determining the biochar properties, such as aromaticity predominantly of biochar, is the pyrolysis temperature (Sohi *et al.*, 2010). In order to reach this temperature, a high amount of energy is required and is consumed in facilities, whether in industrial or laboratory scales. Thus, thorough measures should be adopted for the production and application of biochar to be feasible from an economic point of view. Moreover, due to the fact that pyrolysis is a thermochemical process, during this procedure, emissions such as Polycyclic aromatic hydrocarbons (PAHs) (Resende, de *et al.*, 2018) are produced and without proper measures and treatment, their release will emit the air. Thus, careful and sustainable considerations should also be applied regarding the pyrolysis process from an environmental perspective.

1.3. Energy provision aspect

Although high energy is consumed to provide the required heat for the pyrolyzers to function, the pyrolysis process is not accounted for as an expensive technology. This is due to the emergence of new types of pyrolyzers and the capacity to collect all the byproducts produced aside from biochar. Along with biochar, bio-oil and syngas are also produced. These byproducts can be collected and be utilized as sources of biofuels to provide the required energy as well. However, the yields of the types of byproducts (biochar, bio-oil, and syngas) depend mainly on the type of pyrolysis adopted. For instance, as stated by Laird et al., 2009, in the slow pyrolysis process, the products as biochar, bio-oil, and syngas all have the approximate yields of 35%, 30%, and 30% respectively. Moreover, since pyrolysis is a thermal process, the heat thereafter the production of biochar can be collected from the system and be utilized for other types of purposes. In this case, the isolation of the system with minimum heat loss is essential for the efficient and sustainable consumption of energy. In addition, by the collection of syngas (for instance via the application of the condensation systems), the amount of released emission is eliminated as well and the environmental perspective of pyrolysis process can be also covered (Laird *et al.*, 2009). Another aspect providing the feasibility of the application of biochar and its relevant production process (pyrolysis) is its economic feature.

1.4. Economic perspective

In order for the biochar to be affordable, aside from the required energy for heat provision, the price of the raw feedstock is of high significance. The feedstock utilized for biochar production may interfere with the food production industries and affects the price of food due to rose conflict with this industry over the land occupation (Koide *et al.*, 2015). Thus, the application of biodegradable residues has been mainly pursued as the raw feedstock in biochar production. This application not only may end the conflicts in this regard but also is in complete compliance with sustainable waste management. Moreover, since biochar possesses the C sequestration capacity and its usage as a climate change mitigator, as proposed by Sohi et al., 2010, its application can be entered into the CO_2 trading market according to the Kyoto protocol to supply the biochar more financial support (Sohi *et al.*, 2010). In addition, via the pyrolysis process, some problematic wastes such as the sludges produced from the treatment of the wastewaters, whether industrial or municipal, can be utilized. Previously, the sludges would be collected from the treatment plants and would be transferred and be landfilled. Aside from the expenses of transportation and landfilling of this waste, environmental problems will arise. Consequently, stringent regulations have been established by the authorities hindering the landfilling of such waste without previous and proper treatment (Kamali and Khodaparast, 2015). Another problem in regard to landfilling of sludges is the lack of availability of proper lands for landfilling purposes. Thus, with biochar production, especially with the utilization of such waste, proper waste management along with the elimination of CO_2 release and reduction in expenses of sludge treatment are obtained. Hence, the application of biochar is in complete accordance with the 2030 agenda of sustainable development goals assigned by the United Nations. However, due to varying properties of biochars based on their corresponding feedstock, various experiments are still essential to study the effects and behavior of such additive thereafter its addition into different types of soils.

1.5. The motivation and objectives

The sludge obtained from the treatment of the pulp and paper mill wastewater is considered to be highly problematic. As stated by Kamali et al., 2016, the treatment of such sludge, both the primary and secondary, includes approximately 60% of the total expenses of wastewater treatment of the pulp and paper mill. This sludge is high in quantity and varies in characteristics. This variation in its properties is mainly caused by the usage of different types of raw materials, implementation of diverse processes of pulp and paper production, and last but not least the applied technologies of treating the effluent. The primary sludge is rich in fibrous material, for instance, lignin, metallic compounds, sand, etc. While the secondary sludge contains non-biodegradable components, microbial biomass, decayed cells, etc. This type of sludge can be treated via the utilization of various types of treatment technologies such as anaerobic digestion, activated sludge, membrane bioreactors, etc. (Kamali *et al.*, 2016). These treatment technologies all have benefits and drawbacks. However, all of them are not cost-effective and possess substantial environmental footprints. Another treatment of such sludge can be its conversion into biochar. However, in our best knowledge, there have been limited studies performed in the literature regarding the behavior and effects of such biochar in soil thereafter its addition. Thus, in this study, the biochar produced from the pyrolyzed sludge of pulp and paper mill has been adopted as the amendment and its effects on the physical and chemical properties of the soil were investigated. Moreover, a phytotoxicity experiment was performed to evaluate the influence of this additive in plant growth and the respective crop yield.

2. State of the art

The application of biochar can go back from 500 to 2500 years ago when first applied by ancient Amazonia in Amazon Basin. The first time, in 1542, it was reported by a Spanish wonderer called Francisco de Orellana and the first European who had gone to the center of Amazon, the incredibly fertile soil located there. Further investigations on this land in the 20th revealed that the amount of fertility was anthropogenic. The type of soil covering this area is called “Terra Preta”, a Portuguese name defining as “black earth”. The performed analysis indicated that this type of soil contains a high amount of C due to the addition of biochar produced from manure and fishbone (Laird *et al.*, 2009). Moreover, it was reflected in the literature that the application of biochar was not only the habits of ancient Amazonians. The application of biochar was observed to be practiced in Japan, Africa, South America, Egypt, Greek, and also in the Roman Empire as late as 5000 years ago. The magnificent point is that the Egyptian prolyzers (kilns) are still in use to convert biomass as old tree barks and fruit into biochar via a slow pyrolysis procedure (Semida *et al.*, 2019). Aside from the increase in the C content of the soil amended via biochar, as mentioned earlier in this study, it has been reported in the literature that biochar is empowered to enhance other characteristics of treated soil depending on the applied biochar.

The main alternations in the soil caused by this additive were reported to be the increase of pH (agricultural liming capacity), the CEC, the EC, WHC, the decrease in the bulk density of soil (Nguyen *et al.*, 2017), the enhancement of porosity (Alghamdi, 2018), total stability (Li *et al.*, 2018), the reduction in the released GHGs and the loss of N (Wu *et al.*, 2017), etc. In addition, the biochar has the adsorbing ability which can be utilized as means to immobilize the contaminates and N in the soil (Zama *et al.*, 2018) and, consequently, reduces N leaching and release of N_2O by the microbial community present in soils (Lone *et al.*, 2015). However, these improvements are highly dependent on the applied biochar dosage and its properties. Also, this additive possesses the ability to release of toxic metallic components such as heavy metals into soils. As the plants and the microbial communities are highly sensitive to toxicity, the addition of such an additive may result in negative impacts especially on the crop yield and the microbial community as the bioavailability of released toxins are not determined and specific (Xu *et al.*, 2018) and further they can be accumulated by plants, animals, and eventually humans and cause health problems (Mortensen, Rønn and Vestergård, 2018).

3. Materials and Methods

This study aims to assess some of the physical and chemical alternations in the soil which is caused by biochar produced from the sludge of pulp and paper mill under specific pyrolysis conditions. Moreover, leaching analysis and phytotoxicity tests will be performed to evaluate the toxicity of applied biochar on the germination and the growth of plants. In addition, its effect on the crop yield of the plant will be evaluated. In order to facilitate the comprehension of the role of the biochar, produced from the sludge, as a fertilizer, a comparison with a chemical fertilizer will be also provided to compare the effects of this biochar with another type of commercialized fertilizer.

3.1. Biochar production

In order to proceed with the biochar production, at first the biological sludge from the wastewater treatment of a pulp and paper industry of Portugal, was gathered. The sludge was high in organic content, low in ash content with the moisture content of 89%wb. Then, it was heated in the furnace at a temperature of 105°C for five hours. Thereafter, the dried sludge went through slow pyrolysis in a steel reactor with N_2 as the carrier (inert) gas. The most important pyrolysis conditions adopted for the production are summarized in Table 2. 1. The biochar production was performed in the scope of the project and was not included in this thesis.

Table 2. 1 The adopted pyrolysis conditions for biochar production out of the pulp and paper mill secondary sludge thereafter the biological treatment and dried via a furnace (at temperature of 105°C).

Peak temperature [°C]	Heating rate [°C/minute]	Residence time [minutes]
450	10	120

The pyrolysis steel reactor was designed to have the minimum heat loss and was equipped with a condensation system for the treatment of pyrolysis gaseous pollutions. Figure 2. 1 represents the produced biochar. Thereafter its production, the biochar was smashed and sieved through a 2mm sieve.

Figure 2. 1 The biochar produced from the sludge of pulp and paper mill effluent at the temperature of 450° C and the rate of 10° C/min. The biochar was smashed and sieved through a 2mm sieve.

3.2. Biochar and soil characteristics

The topsoil was and supplied by the pulp and paper industry and collected from its forest soils, was utilized as the soil to be amended with the produced additive. Thereafter, the freshly pyrolyzed product and the collected soil were evaluated regarding their physical and chemical properties.

3.2.1. Physical and chemical characteristics of biochar

In order to analyze the physical and chemical characteristics of the produced biochar, multiple analysis was performed. Table 2. 2 briefly presents the adopted measures and their corresponding purposes. The analysis regarding the biochar characteristics was performed in the scope of the project and they are inserted in this thesis in order to support the general results and the corresponding discussion.

Regarding the physical properties of the biochar as the crystallinity, microstructure, specific surface area (SSA), and porosity of biochar were analyzed. The crystallinity of the biochar was measured via X-ray powder diffraction (XRD) analysis, which is relevant for understanding the aspects of the reactivity of the material. To perform this analysis, the single beam of X-ray has been directed at a specific angle and the angle in which the beam is reflected determines the relevant crystallinity (Aziz *et al.*, 2015) of the biochar. The equipment utilized for this purpose was Rigaku, Geigerflex, Japan and the scanning were continuously performed with the corresponding rate of 2° 2θ/min and varying degrees as 10° to 80° 2θ. Thereafter the produced biochar was analyzed regarding its microstructure structure. To perform such an analysis, the scanning electron microscope (SEM) technique was utilized. This analysis was conducted to determine the morphological aspects of the biochar along with the primary data regarding its surface area and porosity. To perform this analysis a TM4000/TM4000 plus microscope was utilized. Via this analysis, the pore size, the pores distributions, and the corresponding surface roughness of biochar can be determined (Karim *et al.*, 2017). Thereafter, the SSA and the porosity of the biochar samples were evaluated by the gas adsorption method (N_2). The adsorption/desorption isotherms were obtained with a Micromeritics Gemini V2 equipment (USA), and the biochar samples were degassed at 250 ° C for several hours (8 hours) before the measurement. The adsorption data were adjusted to the isothermal equation of Brunauer, Emmett, Teller (BET) to determine the specific surface area of the particles. The method of Barrett, Joyner, Halenda (BJH) was used to estimate the pore size distribution curves.

Table 2. 2 The analysis performed on the pyrolyzed biochar from the sludge in order to determine its chemical and physical properties.

Type of analysis	Analyzed property	Utilized approach
Physical	Crystallinity	XRD
	Microstructure	SEM
	SSA and porosity	Gas adsorption
Chemical	Leaching	Mehlich I & ICP-MS
	Elemental analysis	EDX
	Cl content	XRF
	NH_4^+ and NO_3^- ions	ion chromatography
	C content	analyzer multi N / C®3100 (Analytik Jena AG)
	pH	Extraction (1:5 w/v)
	EC	Filtrated samples of pH measurement

The chemical characteristics of biochar such as its leaching, corresponding elements, Cl content, NH_4^+ and NO_3^- ions, and C content were analyzed separately. The leaching test was performed to evaluate the bioavailability of metals in produced biochar (Li and Shuman, 1997). The extraction method applied was according to Mehlich I method with the corresponding ratio of 1:10 w/v. To perform such analysis, the solutions of 0.05 mol/L of $HCL.H_2O$ (purity of 37% and density of 1.18) with 0.0125 mol/L of H_2SO_4 (purity> 95% and density of 1.83) were adopted as the reagents and then, distilled water was added reaching the total volume of 1L. Thereafter the preparation of such a solution, 10mL of such solution was added into a falcon tube with one gram of biochar (450°C with the rate of 10°C/min) which has been previously smashed and sieved into 2mm of a sieve. For this analysis, three replicates were adopted. Afterward, such a solution was stirred for 5 minutes with the corresponding speed of 15rpm. Subsequent to the shake, the samples were stood for 16 hours and they were filtered via a vacuum filtration

(Bissani *et al.*, 2002). Afterward, the samples in the volume of 10 mL were analyzed via an inductively coupled plasma mass spectrometry (ICP-MS) technique. Then, the prepared samples were analyzed via ion chromatography technique (Dong *et al.*, 2016). The chosen elements for such an analysis were as Ca, Na, K, P, Cu, Mg, Ni, Pb, Fe, Zn, Al, Cr. Figure 2. 2 represents the stage in which the samples were being stirred. Further on, the obtained concentrations in mg/L will be converted into mg/kg via the application of Equation 2.1.

$$\text{element concentration } \left(\frac{g}{kg}\right) = \frac{\text{concentration } \left(\frac{mg}{L}\right) \times \text{volumeof the solution (mL)} \times 10^{-6}}{\text{mass of the sample (kg)}} \quad \text{Equation (2.1)}$$

Regarding the elemental analysis of produced biochar, the EDX analysis was performed. This analysis was performed along with the SEM analysis and via the application of X-rays as the utilized signals (Wang, Wang and Wang, 2018). To evaluate the biochar regarding containing Cl content, the X-ray fluorescence spectroscopy (XRF) analysis was performed on 1g of smashed and sieved (2mm) biochar. The NH_4^+ and NO_3^- ions of produced biochar was tested via the application of ion chromatography. For sample preparation, NH_4^+ and NO_3^- ions were extracted in the ratio of 1:10 (w / v) with KCl in 15 mL Falcon tubes in the dark on a shaker at 150 rpm at room temperature (22ºC ± 3 ° C) for 2 hours. The samples were then filtered to separate the biochar extracts using vacuum filtration.

Figure 2. 2 The preparation of samples for leaching analysis. In this stage, the samples have been stirred for 5 minutes on the stirrer with the relative speed of 250 rpm. Three replicates has been adapted for each condition.

Moreover, the C content of the produced biochar was analyzed with analyzer multi N / C®3100 (Analytik Jena AG). In this method, the recorded amount of biochar was inserted into ceramic boats and they were inserted in the heating tunnels. Figure 2. 3 represents the biochar in the ceramic boats. Then, the sample was heated up to 1300°C and the amount of total inorganic carbon (TIC) was obtained. By subtraction from the total amount, the amount of total organic carbon (TOC) was obtained.

Figure 2. 3 The biochar, produced with the maximum temperature of 450°C with the rate of 10°C/min, in ceramic boats for TIC analysis.

The corresponding pH of the produced biochar was also measured according to the international standard of ISO 10390 (International Organization for Standardization, 2005). In this regard, the biochar was extracted in the ratio of 1:5 (w/v), and the distilled water was considered as the reagent. For the determination of pH, three replicates of samples were prepared. After being stirred for 2 hours with the caps on, the corresponding pH of the samples was measured after the calibrating the pH meter and while again being stirred via a magnetic stirrer. Thereafter the measurement of the pH, the samples were filtered with the vacuum filtration, and their corresponding EC was measured. The performed procedure for EC measurement was in compliance with the international standard of ISO 11265 (International Organization for Standardization, 1994).

3.2.2. Properties of soil

The supplied soil by the pulp and paper industry was left for three days in a big container to be air-dried. Thereafter the soil being air-dried, it was sieved through a 2mm of a sieve to have a homogenous structure, represented in Figure 2. 4. Then, the corresponding structure and its elemental characteristics were analyzed via SEM and Energy-dispersive X-ray spectroscopy (EDX) techniques. Moreover, the prepared soil was analyzed regarding its moisture content according to the international standard of ISO 11465 (International Organization for Standardization, 1993). In this regard, 5g of soil was weighed and its corresponding weight was recorded. Then, it was inserted into a furnace at a temperature of 105°C ± 5°C for five hours. Afterward, its corresponding weight was recorded and was subtracted from the original weight. The obtained amount is the respective amount of soil moisture. The leaching test was also applied for the soil with three replicates according to Mehlich I method which has been described previously.

Figure 2. 4 The soil supplied by the pulp and paper industry and collected from its forest soils. The soil was air-dried for three days and then it was sieved through a 2mm sieve.

Moreover, the corresponding pH and EC of the collected soil were measured according to the international standards of ISO 10390 (International Organization for Standardization, 2005) and 11265 (International Organization for Standardization, 1994) respectively, which has been described previously. In addition, the WHC of the collected soil was measured according to Annex A of the international standard of ISO 14240 (International Organization for Standardization, 1997). However, in order to perform this analysis, the filter Crucibles, also known as Gooch crucibles, with 2mm pores were utilized. In order to obtain the WHC of the filters of the containers, after weighing the containers, 2mL of water was poured on their filters and then they were shaken and weighed again. The subtracted amount from these two measurements represents the WHC of the filter of each container. Moreover, 50g of air-dried soil was inserted in each of the containers. Then, the containers were placed in a vessel with water, for two hours at room temperature, to become soaked until the top sample. Then, the containers with the soaked samples were placed on top of a drain and left to drain for 2 to 24 hours, with the cover over them to eliminate evaporation. Afterward, the containers were weighed, and they were inserted in the furnace at a temperature of 105°C ± 5°C for 24 hours. Consequently, they were taken out and were inserted into a desiccator for one hour and then they were weighed, and their corresponding weights were recorded. By subtracting the initial weight (after being drained), the dry weight (after being kept in a desiccator), and the WHC of the filters, the corresponding amount of WHC of soil is obtained. The whole procedure is represented in Figure 2.5.

Figure 2. 5 The adopted procedure to measure the WHC of the soil supplied by the pulp and paper industry (with the utilization of 3 replicates).

3.3. Incubation

In order to evaluate the long-term effects of the biochar addition in the soil, the incubation experiment was conducted according to the European Standard of EN 14984 (European Standard, 2006). In order to provide a comparison with the effects of biochar additive, which are assumable to have on the soil, another additive which is commercially used corrective agricultural compound (designated Biocal) containing mainly consisting of $CaCO_3$ (chemical additive) was also added with the same doses in separate samples. The adopted rates of additive doses were chosen to be 0 (incubated soil), 2.5, 5, and 10% (w/w). For each additive, three replicates were prepared. The samples were kept at 80% of the WHC of the soil for the duration of 21 days, in the constant temperature of 20°C ± 1°C, and darkness. The samples were kept in black plastic bags and loosely they were closed with air inside due not to eliminate air exchange and also to minimize the moisture loss. Figure 2.6 presents the conditions in which the samples were kept. Moreover, in order to assess the effect of small doses of biochar, two more dosages as 0.5% and 1% w/w of incubated samples with the similar incubation criteria (80% of WHC and 21 days as the duration of the incubation) were applied with three replicates for each condition.

Figure 2. 6 The conditions in which the soil with biochar and $CaCO_3$ additives were kept during the incubation (with 3 replicates for each condition).

Every seven days, during the incubation period, the samples were taken out of the incubator, airy and the corresponding pH, EC, and WHC were measure. The adoption of 21 days for the period of incubation was due to the fact that after this period the properties of the samples reached a semi-stable stage.

3.3.1. pH

The pH of the samples was measured under the international standard of ISO 10390 (International Organization for Standardization, 2005) (described previously). Figure 2.7 illustrates the stages applied to the pH measurement of incubated samples.

Figure 2. 7 The adopted steps for the pH measurement of incubated samples (soil as received, soil amended with biochar with doses of 0.5, 1, 2.5, 5, and 10% w/w, and soil with the commercial fertilizer containing mainly $CaCO_3$ with doses of 2.5, 5, and 10% w/w). For this measurements, 3 replicates has been applied for each condition.

3.3.2. Electrical conductivity

The corresponding EC of the samples was analyzed according to the international standard of ISO 11265 (International Organization for Standardization, 1994) (described previously).

3.3.3. Water holding capacity

The WHC of the samples was evaluated based on Annex A of the European standard of EN 14240 (European Standard, 2006) (according to the applied above-mentioned details). Figure 2.8 illustrated the adopted stages for the performance of this analysis.

Figure 2. 8 The adopted procedures in order to measure the WHC of the incubated samples, incubated soil, soil amended with biochar (2.5, 5, and 10% w/w), and soil amended with the commercial fertilizer containing mainly $CaCO_3$ (2.5, 5, and 10% w/w) (with three replicates for each condition).

3.3.4. Leaching

Thereafter the duration of the incubation, i.e. 21 days, the samples as the incubated soil, the soil as received (air-dried and sieved), and the soil amended with biochar with doses of 2.5, 5, and 10% w/w, were extracted with Mehlich I method (with the specification mentioned above). After the filtration of the samples with vacuum filtration, they were analyzed regarding the bioavailability of their metallic compounds via the ICP-MS technique. Similarly to the leaching test applied for the biochar alone, the elements adopted for this analysis were as Ca, Na, K, P, Mg, Fe, Zn, Al, and Cr.

3.4. Phyoxicity test

To evaluate the phytotoxic behavior of the produced biochar in the soil, after the incubation test, two phytotoxicity analysis of the germination test and the growth test were performed.

3.4.1. Germination test

The germination test analyzes the germinating ability of the seeds in the provided conditions (Zocconi *et al.*, 1981). In order to perform this analysis, the incubated samples of soil and soil amended with biochar were extracted in the ratio of 1:5 (w/v) with distilled water and by being stirred with the speed of 200 rpm. Figure 2.9 represents the extracted samples. Then, the extracted samples were filtered via vacuum filtration and dilutions of 30%, 60%, and 100% (v/v) were prepared from each type of condition (incubated soil, incubated soil amended with biochar of 2.5, 5, and 10% w/w). Moreover, *Lepidium sativum* was chosen as the germination seed test. This plant was selected to perform this analysis due to its sensitivity towards the environmental conditions to germinate and also for its fast rate of germination. In this regard, three petri dishes (with the approximate diameter of 100mm) with the one filter paper inside each, were prepared for each condition of incubated samples. Moreover, 5 additional petri dishes were also prepared similarly to be as the control samples with only the 2mL of distilled as the main solution. In each petri dish, the number of 10 seeds of *Lepidium sativum* was inserted. Over the seeds on the filter papers, the 2mL of prepared solutions were poured via the pipet (±0.05 mL). Figure 2. 10 illustrates the prepared petri dishes previous to the addition of solutions.

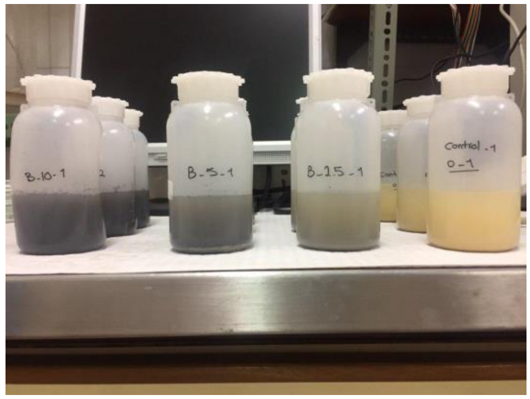

Figure 2. 9 The extracts of incubated samples of soil and amended soil with 2.5, 5, and 10% (w/w) of biochar additive (with 3 replicates for each condition).

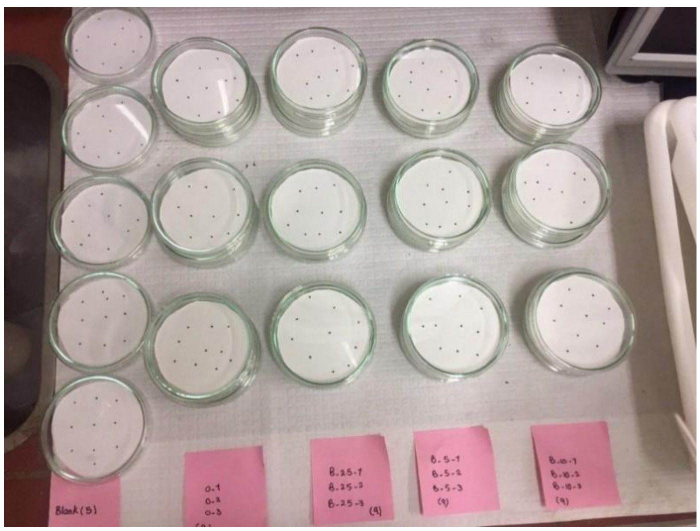

Figure 2. 10 The prepared petri dishes with a filter paper and 10 seeds of *Lepidium sativum* (with 5 replicates for the control and 3 replicates for each condition).

Thereafter the sample preparations, the petri dishes were kept in an incubator with a constant temperature of 28°C and in darkness for the duration of 24±12 hours. Figure 2. 11 represents the incubator in which the petri dishes were kept inside. The samples were checked after the duration of incubation (30-34 hours) and were taken out of the incubator for further analysis. Each replicate was analyzed regarding the number of its germinated seeds and the length of the roots. Then, the germinated seed percentage (G%) was calculated according to Equation 2.2.

$$G\% = \frac{number\ of\ germinated\ seed\ in\ each\ extract}{number\ of\ germinated\ seed\ in\ control} \times 100 \qquad \text{Equation (2.2)}$$

Moreover, the root length percentage (L%) of each condition was calculated via Equation 2. 3 thereafter the measurement. Figure 2. 12 represents the measurement of the roots. To conduct the measurement, the seeds were taken out of the petri dishes and the sprouts were measured under a magnifying glass with a ruler.

Figure 2. 11 The prepared petri dishes with ten seeds of *Lepidium sativum* and 2mL of extracts of incubated samples (soil and amended soil with 2.5, 5, and 10% 9w/w) (with 3 replicates for each condition), plus five dishes as control (as the replicates).

$$L\% = \frac{mean\ root\ length\ in\ each\ extract}{mean\ root\ length\ in\ control} \times 100$$

Equation (2.3)

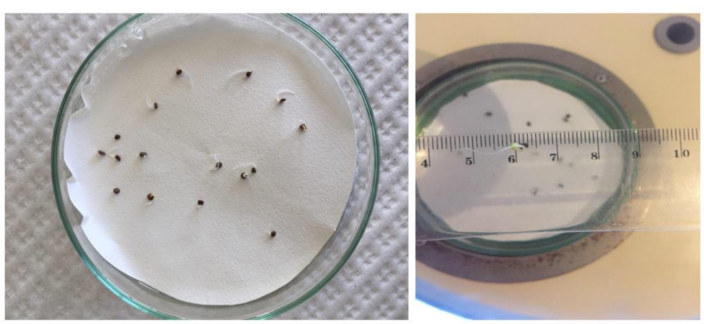

Figure 2. 12 The measurement of the germinated seeds via a ruler. The average root of the germinated seeds was further be utilized for calculation of the length percentage corresponding

to the phytotoxicity analysis on the soil and the amended soil with biochar (doses of 2%%, 5%, and 10%).

Thereafter the calculations of G% and L%, the germination index (GI%) of samples can be obtained via Equation 2.4.

$$GI\% = \frac{G\% \times L\%}{100} \qquad \text{Equation (2.4)}$$

The GI% communicates to which degree the provided condition is toxic for plant germination and growth. The GI% over 60% (GI%>60%) represents the non-toxicity factor of the utilized amendment. After the calculation of the GI%, the obtained results will be analyzed via the one-way analysis of the variances (one-way ANOVA) analysis to determine the significant differences among the obtained results.

3.4.2. Growth test

To evaluate the effects of biochar on the growth of the plant a growth test was adopted. Six plastic pots were prepared for each of the conditions, i.e. the soil as received (air-dried and sieved through a 2mm sieve), incubated soil, soil amended with biochar (with doses of 2.5, 5, and 10% w/w), and soil amended with commercial corrective agricultural compound (liming agent) containing mainly $CaCO_3$ (with doses of 2.5, 5, and 10% w/w). In each pot, a small transparent plastic bag was inserted, and the pots were labeled. To proceed with this test, *Lolium perenne* seeds were selected due to their rapid rate of growth and the short duration of life. Moreover, this plant was adopted as the test plant due to its insensitivity towards the metallic contaminations in soil, and by the metal accumulation, its growth will not be eliminated (Norini *et al.*, 2019). To test the health of seeds a germination analysis was performed via the application of a dish, cotton, and distilled water. Twelve seeds were inserted on the wet cotton in a dish and kept in darkness for the duration of seven days. Figure 2. 13 represents the performed test on the health of the *Lolium perenne* seeds. Then, 150g (db) of each condition was put in each pot. Twenty seed of *Lolium perenne* was planted in the approximate distance of 5mm from the topsoil. Figure 2. 14 illustrates the seed plantation.

Figure 2. 13 The germination test performed on the *Lolium perenee* seeds to evaluate their health for further growth test to evaluate the effects of biochar additive on the plant germination in soil, growth, and their corresponding yield.

Figure 2. 14 Twenty seeds of *Lolium perenne* were planted in the approximate 5mm distance from the topsoil in each pot containing different conditions, i.e. soil as received, incubated soil, amended soil with biochar (2.5, 5, and 10% w/w), amended soil with commercial corrective agricultural compound containing mainly $CaCO_3$ (2.5, 5, and 10% w/w) (with 6 pots for each condition as the replicates).

Moreover, to evaluate the germination in the soil as collected and the growth of the plant with the amended soil with biochar another condition was created. In this condition, 100g (db) of soil amended with biochar with a dose of 5% w/w was considered as the bottom soil and then 50g (db) of soil as received was put as the topsoil. Similarly, 20 seeds of *Lolium perenne* were planted in the approximate distance of 5mm from the surface of the soil. On the first day of the plantation, all the pots were irrigated with 60% of their corresponding WHC according to their condition. Afterward, the pots were weighed daily and the amount of water, which they had lost due to evaporation, was added to each pot. After the germination was finalized, every three pots of each condition (from the six replicates), was irrigated with a 0.6 mL of N solution (NH_4NO_3 with the concentration of $4gNH_4NO_3/100mL$) every two days in a row to evaluate the effect of N addition on the growth. Figure 2. 15 illustrates the applied pots with the seeds planted.

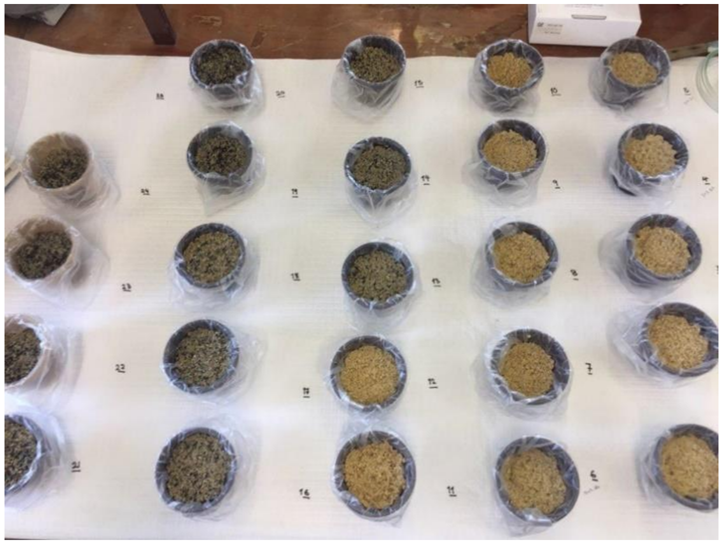

Figure 2. 15 The applied growth test to evaluate the effect of biochar addition on the growth and crop yield of *Lolium perenne*. For each condition, i.e. the soil as received, the incubated soil, the amended soil with biochar (2.5, 5, and 10% w/w/), and the soil amended with commercial corrective agricultural compound containing mainly $CaCO_3$ (2.5, 5, and 10% w/w), 6 replicates were conducted. However, for the special condition, i.e. 100g (db) of amended soil with biochar of 5% w/w dose and 50g (db) of soil as received as topsoil, only 3 replicates were considered.

3.4.2.1. Germination

During the following four days from the plantation of the seeds, the pots were closely monitored for the germination of the seeds. The corresponding number of germinated seeds of each pot was counted and were recorded on a daily basis. At the time that the average of more than 50% of the seeds of each condition was germinated, it could be concluded that the germination had been stopped and the germination duration of the seeds in each condition could be obtained. Figure 2. 16 represents the germinated seeds in two different conditions (incubated soil and amended soil with biochar 5% w/w) at the early stage.

Figure 2. 16 The first germinated seeds observed in two conditions (incubated soil (a) and amended soil with biochar of 5% w/w (b)). Every day the number of germinated seeds of each condition was precisely counted and were recorded.

3.4.2.2. Growth

At the time that the germination was concluded to be stopped in each condition, continuously, the growth test could be carried out. The duration of the growth test was considered to be approximately 15 days. In this experiment, the growth chamber was not utilized, and the pots were kept in the room temperature (20°C±5°C) and were placed under the direct sunlight. Moreover, during the nights, the light was kept on facilitating the growth of the plants. The length of the leaves (green stalks growing over the topsoil) of each condition was measured on a daily basis via the ruler and was recorded. Figure 2. 17 represents the performed measurement on one of the conditions. Thereafter, at the time when the length of the leaves reached a semi-fixed size, the growth test was considered to be finished.

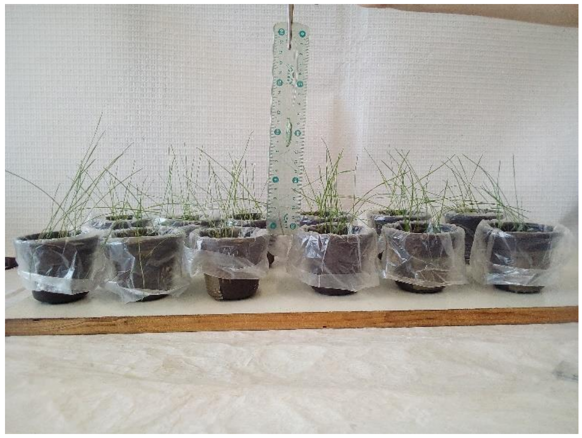

Figure 2. 17 The length of the leaves of each condition was measured via a ruler on a daily basis during the conduction of the growth test.

3.4.2.3. Yield

Thereafter the conduction of the growth test, the crops were collected from each condition while they were still attached to the roots, and the soil attached to them was removed. Then, their corresponding length of leaves and roots were measured via a ruler (demonstrated in Figure 2. 18). Moreover, the roots and the leaves were separated from one another and were stored in separate dishes (represented in Figure 2. 19).

Figure 2. 18 The crops from each condition are collected and their corresponding length of roots and leaves are measured via rulers and are recorded.

Figure 2. 19 The collected leaves of each condition are separated from their roots and both the leaves and the roots are stored in separate labeled dishes.

In addition, the collected leaves from each condition were inserted in a furnace at a temperature of 105°C ±5°. Every five hours, they were taken out of the furnace and were weighed and till a fixed weight corresponding to the leaves of each condition was obtained they were kept in the furnace (at 105°C ±5°). Thereafter the achievement of a stable weight (db) of leaves of each condition, they were weighed for the last time and their corresponding weights were recorded. Further on, the dried leaves will be stored in a desiccator. Accordingly, the three parameters of the yield as; i) dry weight of the leaves, ii) crop heights, and iii) the root development of each condition were obtained. Further on, based on the crop parameter, the best condition affecting and increasing the crop yield the most can be determined.

4. Results

4.1 Soil and biochar characteristics

4.1.1. Biochar characteristics

Primarily, the results regarding the physical and chemical properties of the biochar, which is produced from the biological sludge from the wastewater treatment of a pulp and paper industry at the pyrolysis condition of 450°C as the maximum obtained temperature, 10°C/min as the rate of pyrolysis, and the duration of two hours, are represented. The pH and EC of the produced biochar were measured to be respectively 8.4 and 3.4 mS/cm.

The microstructure analysis performed on the biochar via the application of SEM analysis resulted in Figure 2. 20. As it can be observed from this figure, the produced biochar possesses an irregular microstructure while it is highly porous.

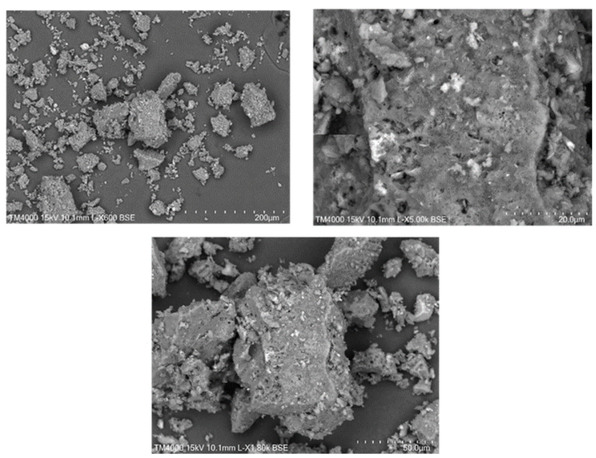

Figure 2. 20 The microstructure of the produced biochar analyzed via the application of the SEM technique. It possesses an irregular structure and it is porous.

Thereafter the calculation of the specific surface area (SSA) and the porosity analysis on the produced biochar via the application of the N_2 adsorbing technique, the following results were obtained. The amount of the ratio of adsorbed/desorbed amount of the N_2 was observed to be less than 4mmol/g determining that its SSA is relatively low. The hysteresis curve in this regard is provided in Figure 2. 21. Moreover, the BET area, the corresponding pore size, and pore volume of the produced biochar were obtained to be 2.16 m^2/g, 0.005052 cm^3/g, and 130 Å (nm), respectively. The summary of the obtained results in this regard is presented in Table 2. 3.

Table 2. 3 The adsorbed/desorbed ratio, SSA, pore volume, and pore size of the produced biochar obtained from the conduction of N_2 adsorbing technique.

Sample	Adsorbed/desorbed (mmol/g)	BET area (m^2/g)	Pore volume (cm^3/g)	Pore size (Å)
Biochar (450°C, 10°C/min)	<4	2.16	0.005052	130

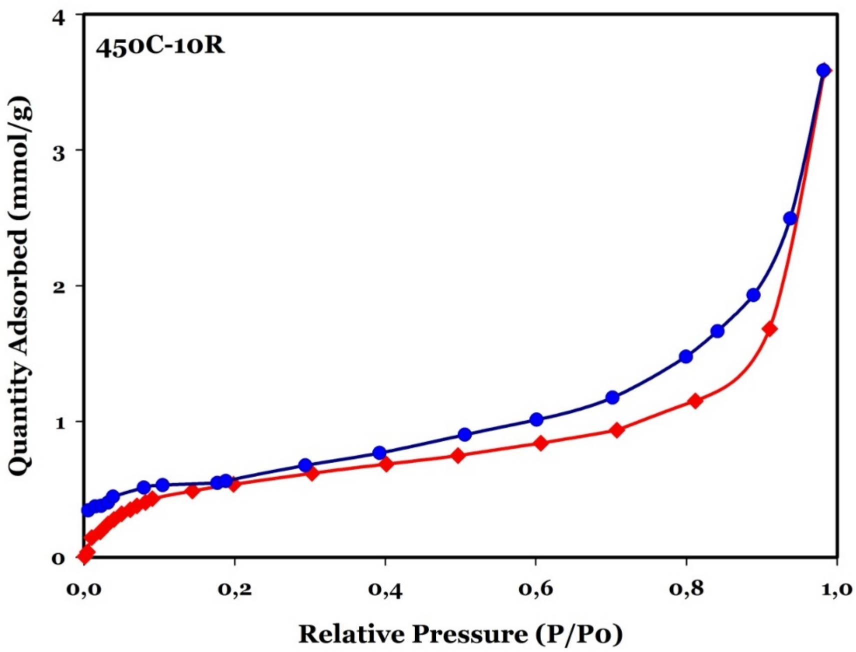

Figure 2. 21 The hysteresis curve of the biochar produced. This figure represents that the ratio of the adsorbed/desorbed of N_2 is less than 4mmol/g. Thus, the SSA of the produced biochar is low.

Thereafter the conduction of the ion chromatography technique, the amount of NO_3^- of the produced biochar under the implemented pyrolysis conditions (450°C as the peak temperature, 10°C/min as the pyrolysis rate, and 2 hours as the residence time) from the biological sludge from the wastewater treatment of a pulp and paper industry was calculated to be 10 gNO_3^-/ kg of produced biochar. Also, the Cl content of the produced biochar (via the application of XRF analysis) was observed to possess a percentage of 1.55%. Moreover, the total carbon (TC) of the produced biochar was calculated to be 460 g C/kg biochar (with total organic carbon (TOC) of 450g C/kg biochar and 10g C/kg biochar as the total inorganic carbon (TIC)). Thus, the produced biochar contains mainly organic C. Table 2. 4 briefly demonstrates the obtained characteristics of the produced biochar.

Table 2. 4 The summary of chemical properties of the produced biochar such as the nitrate content, chlorine content, and carbon content (whether organic and inorganic).

Sample	NO_3^- (g nitrate/kg biochar)	Cl^- (%)	TC (g C/kg biochar)	TOC (g C/kg biochar)	TIC (g C/kg biochar)
Biochar (450°C, 10°C/min)	10	1.55	460	450	10

In addition, according to the measurements performed via the EDX analysis, it was comprehended that the produced biochar contains elements as Fe, S, Si, Cl, Al, and P. Figure 2. 22 represents the obtained results from the EDX analysis performed on the produced biochar. However, from this analysis, the C content of the produced biochar cannot be determined due to the fact that a thin layer of graphite (C) is applied to the samples to perform the analysis. Thus, the addition of the graphite interferes with the observation of the C content of the samples.

The results achieved from the XRD analysis are provided in Figure 2. 23. As it can be observed from this figure, the produced biochar mainly contains $CaCO_3$, SiO_2, and $KAlSi_2O_6$, with the respective percentages of 41%, 33%, and 26%. Table 2.5 presents the relative scores corresponding to the compounds with the highest concentrations. Moreover, the utilized reference codes applied to distinguish the compounds mainly present in the produced biochar are also represented in this table.

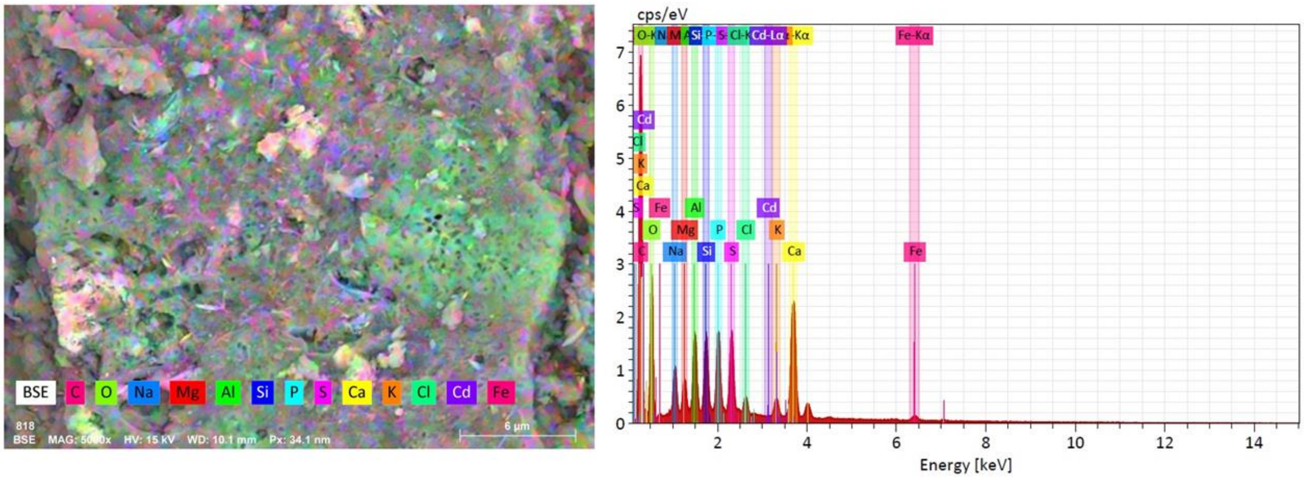

Figure 2. 22 The EDX analysis performed on the produced biochar representing concentrations of elements as Fe, S, Si, Cl, Mg, Al, and P.

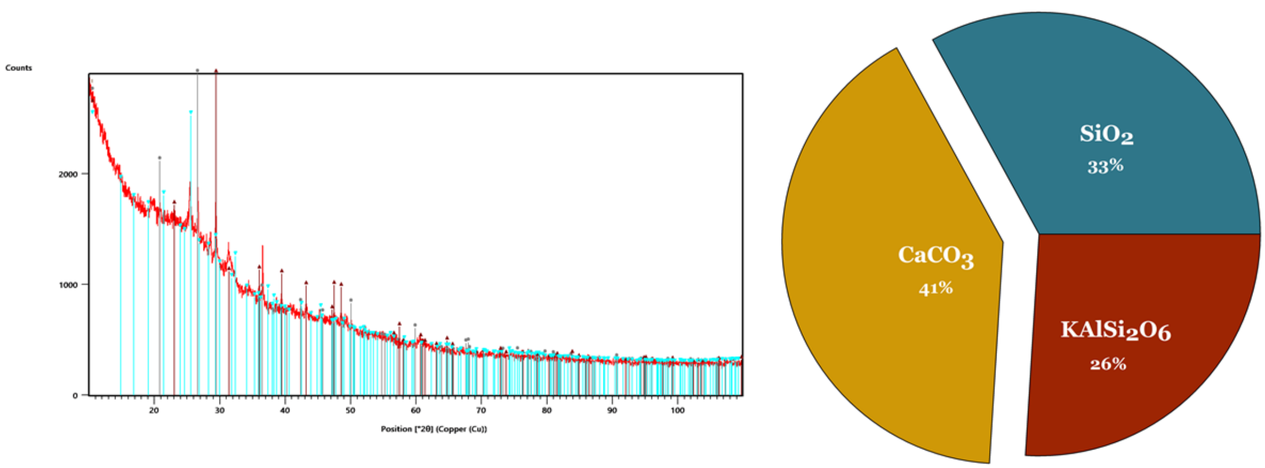

Figure 2. 23 The obtained results from the XRD analysis performed on the produced biochar. The results demonstrate that the biochar mainly contains $CaCO_3$, SiO_2, and $KAlSi_2O_6$.

Table 2. 5 The obtained results from the XRD analysis performed on the produced biochar. The corresponding percentage, scores, and the used reference codes for the determination of the compounds ($CaCO_3$, SiO_2, and $KAlSi_2O_6$) are provided.

Ref.Code	Score	Compound Name	Scale Fac.	Chem. Formula
01-089-1961	24	Silicon Oxide	0.749	SiO_2
01-080-9776	19	Calcium Carbonate	0.690	$Ca(CO_3)$
04-012-1907	4	Potassium Aluminum Silicon Oxide	0.379	$KAlSi_2O_6$

The leaching of the elements as Ca, Na, K, P, Mg, Ni, Pb, Fe, Zn, Al, and Cr, which was conducted via the Mehlich I approach and measured via the ICP-MS analysis, from the produced biochar are provided in Table 2.6. Accordingly, the most bioavailable elements with the high leaching potential among the analyzed elements in the produced biochar are Ca, Na, and K. Moreover, the concentrations of elements as Ni, Cu, and Pb were below the detection limits and consequently, they were not presented in Table 2.6.

Table 2. 6 The leaching amounts of elements as Ca, Na, K, P, Mg, Fe, Zn, Al, and Cr from the produced biochar under specific conditions. The symbol "-" in the table represents that the corresponding value was below the measurement detection limit and it was too little to be detectable via this method.

condition	Ca g/kg	Na g/kg	K g/kg	P g/kg	Fe g/kg	Mg g/Kg	Zn g/kg	Al g/kg	Cr g/kg
Biochar (450°C, 10°C/min)	10.769	8.5324	3.276	0.574	-	1.0123	-	0.0022	-

4.1.2. Soil characteristics

The results obtained regarding the chemical and physical properties of the air-dried and sieved (2mm) soil supplied by the pulp and paper industry, are provided as follows. The collected soil possesses a relative moisture content of 1.68 gH_2O/kg air-dried soil. The corresponding WHC of the air-dried soil was measured to be 210.54 g/kg. The pH and the EC of the soil were measured to be 4.92 and 80.7 µS/cm, respectively. Table 2.7 briefly summarizes the obtained results regarding the soil characteristics.

Table 2. 7 The properties such as pH, EC, WHC, and moisture content of air-dried and sieved (2mm) supplied soil.

Sample	pH	EC (µS/cm)	WHC (g/kg)	Moisture content (gH_2O/kg)
Air-dried and sieved soil	4.92	80.7	210.54	1.68

The results regarding the elemental leaching (Ca, Na, K, P, Mg, Ni, Pb, Fe, Zn, Al, and Cr) of the soil as received are presented in Table 2.8.

Table 2. 8 The leaching amounts of elements as Ca, Na, K, P, Mg, Fe, Zn, Al, and Cr of the supplied soil. The analyzed soil was air-dried (3 days) and sieved (2mm). The symbol "-" in the table represents that the corresponding value was below the measurement detection limit and it was too little to be detectable via this method.

Sample	Ca g/kg	Na g/kg	K g/kg	P g/kg	Fe g/kg	Mg g/Kg	Zn g/kg	Al g/kg	Cr g/kg
Soil as received	0.0899	0.31366	-	-	0.009	-	-	0.0405	-

Moreover, regarding the microstructure and the chemical properties of the soil, the obtained results from the SEM and EDX analysis are provided. Figure 2. 24 demonstrates the microstructure of the soil. As it can be observed from this figure, the soil has an irregular microstructure. As can be observed from this figure, the soil is not considered to be porous.

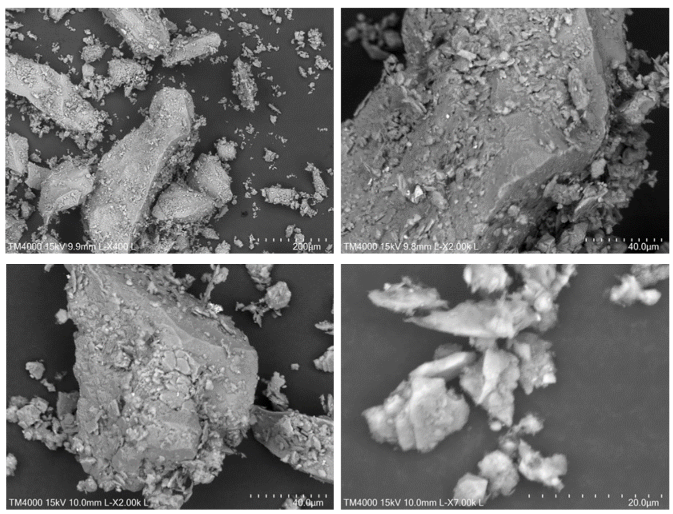

Figure 2. 24 The microstructure of the supplied soil obtained from the SEM analysis. The soil has an irregular microstructure.

In addition, the EDX analysis performed on the collected soil, which was further air-dried and sieved through a 2mm sieve, demonstrates that the soil is rich in O, Si, Al, and Fe. The amount of C presented is due to the thin layer graphite applied for the purpose of this analysis and the soil is poor in element C. The obtained results in this regard are presented in Figure 2. 25.

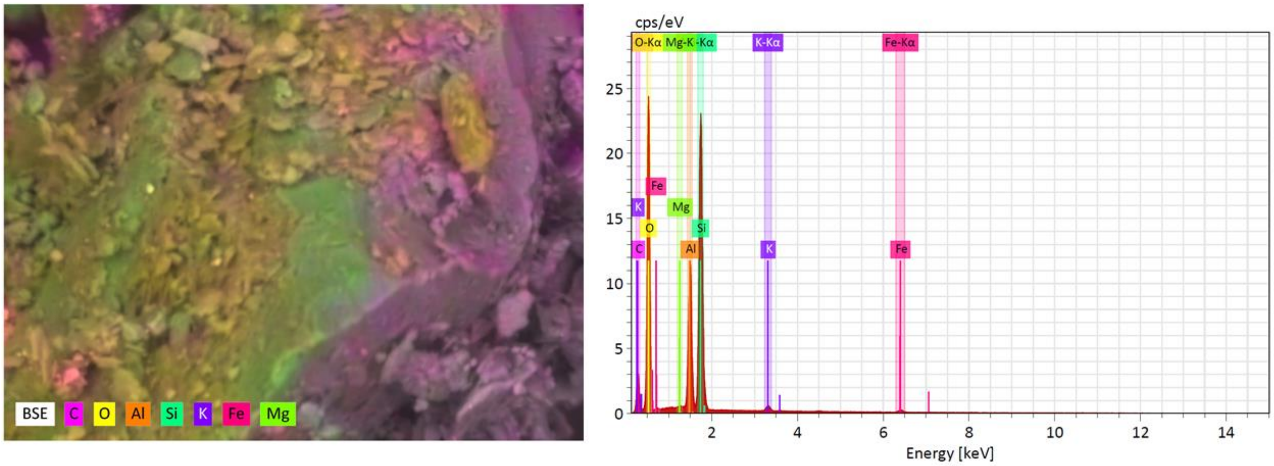

Figure 2. 25 The obtained results from the EDX analysis performed on the supplied soil. The soil is rich in elements as O, Si, Al, and Fe. However, the amount of element C corresponding in the soil is quite low and the amount of C demonstrated in this figure is mainly due to the graphite thin layer applied for the purpose of this analysis.

4.2. Incubation

During the incubation test, which was 21 days, the incubated samples were weekly analyzed regarding their corresponding pH, EC, and WHC. The obtained results in this regard are presented as following. Moreover, thereafter the duration of the incubation (21 days), it was observed that the amended soil with biochar had gotten darker in color and the extend of the darkness was dependent on the dose of applied biochar, i.e. the amended soil with the biochar of 10% w/w possessed the darkest color.

4.2.1. pH

The initial pH considered for all the conditions as in day zero was considered to be the pH of the air-dried soil as 4.92. Table 2.9 represents the pH alternations throughout the incubation duration of 21 days for all the incubated conditions (incubated soil, amended soil with biochar with doses of 0.5% (B 0.5%), 1% (B1%), 2.5% (B2.5%), 5% (B5%), and 10% (B10%) w/w, and incubated soil with the commercial liming agent containing mainly $CaCO_3$ (chemical additive) with doses of 2.5% (C2.5%), 5% (C5%), and 10% (C10%) w/w). Moreover, for better visualization, the corresponding pH of all the conditions is demonstrated in different figures. Figure 2. 26 demonstrates the alternation of biochar additive with doses of 0.5% and 1% on the soil pH throughout the 21 days (incubation period). The biochar additive with the doses of 0.5% and 1% altered and increased the pH of the soil to 7.13 and 7.33, respectively, after three weeks.

Table 2. 9 The variation of the pH from the incubation and the soil additives as the biochar and the chemical additive ($CaCO_3$) during the incubation duration of 21 days.

Duration (days)	Analyzed parameter	Incubated soil	B 0.5%	B1%	B2.5%	B5%	B10%	C2.5%	C5%	C10%
7		5.3	7.27	7.47	7.92	8.13	8.42	8.21	8.41	8.39
14	pH	5.31	7.11	7.59	7.97	8.22	8.43	8.19	8.12	8.37
21		5.29	7.13	7.41	7.71	7.95	8.19	8.17	8.24	8.25

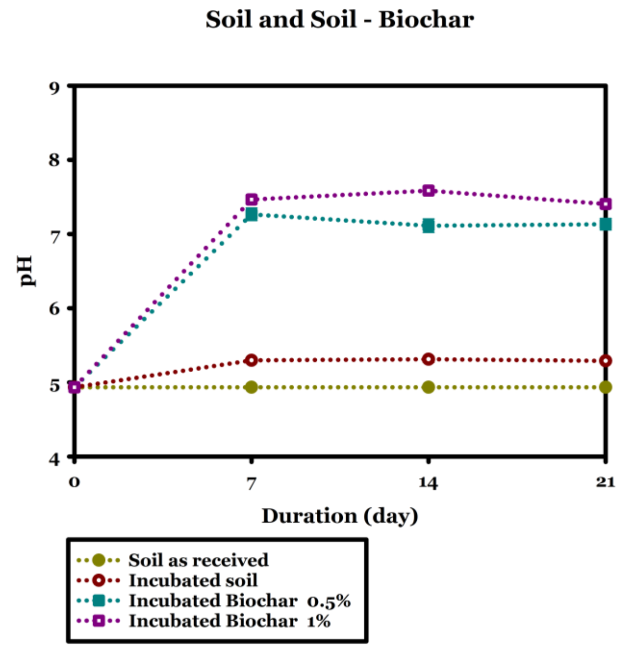

Figure 2. 26 The pH alternation of soil amended with biochar with doses of 0.5% and 1% w/w, produced under certain conditions (from the secondary sludge, with the peak temperature of 450°C and the corresponding rate of 10°C/min) through the incubation test with the duration of 21 days and 3 replicates for each condition.

The biochar additive with the doses of 2.5%, 5%, and 10% w/w also increased the pH of the soil to 7.71, 7.95, and 8.19, respectively, after 21 days as the duration of the incubation. Figure 2. 27 demonstrates the alternation of the pH of the soil caused by the different doses of biochar additive throughout the 21 days as the incubation period.

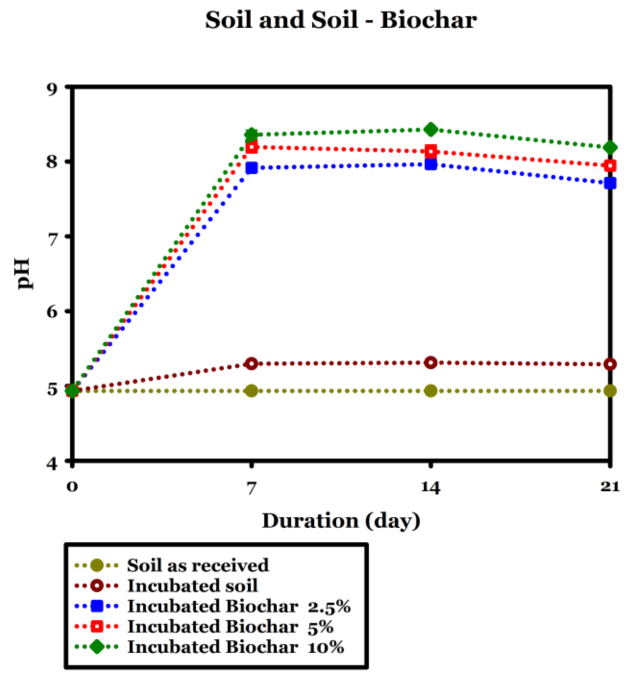

Figure 2. 27 The pH alternation of soil amended with biochar with doses of 2.5%, 5%, and 10% w/w, produced under certain conditions (from the secondary sludge, with the peak temperature of 450°C and the corresponding rate of 10°C/min) through the incubation test with the duration of 21 days and with 3 replicates for each condition.

In addition, the liming agent mainly containing the $CaCO_3$ also enhanced the pH of the soil. However, it was comprehended that with smaller doses of this additive higher pH can be obtained in comparison with the biochar additive. Moreover, no noteworthy difference has been caused in the pH of the amended soil with different doses of the $CaCO_3$ additive as in all the conditions amended with the $CaCO_3$, the pH of approximately 8 was obtained. Figure 2. 28 illustrates the pH variation during the incubation period caused by the $CaCO_3$ additive with doses of 2.5%, 5%, and 10% w/w.

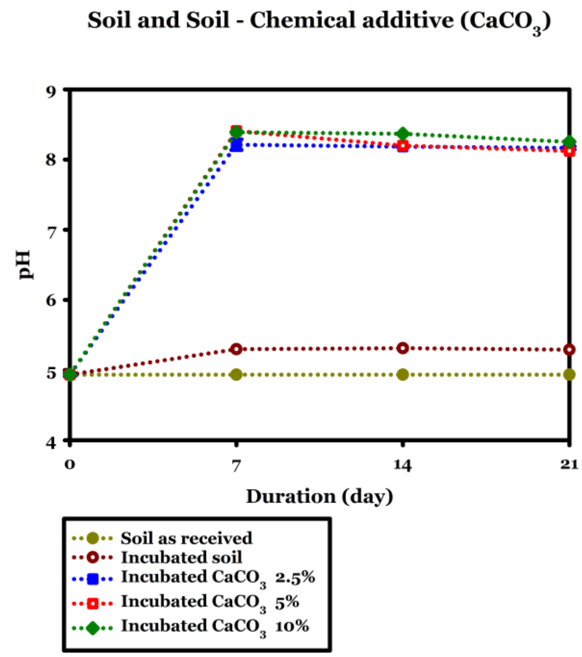

Figure 2. 28 The pH alternation of soil amended with the liming agent containing mainly $CaCO_3$ through the incubation test with a duration of 21 days and with 3 replicates for each condition.

Thereafter the conduction of the pH analysis on the incubated samples it was comprehended that; i) the incubation did not affect the soil pH as no considerable modification was observed in the incubated soil, ii) the small doses of biochar as 0.5% and 1% w/w have the capacity to apply pH correction of the soil, and iii) with smaller doses of the chemical additive ($CaCO_3$) higher pH can be obtained in comparison to the biochar additive with the similar doses.

4.2.2. Electrical conductivity

The EC was another parameter which was measured on a weekly basis in all the incubated samples. Table 2. 10 represents the corresponding measured EC of the incubated samples throughout the incubation period of 21 days. The initial EC considered for all the incubated samples as a day zero was assumed to be similar to the EC of the soil as received (80.7 µS/cm). Moreover, for better visualization, different figures illustrating the variation in the EC of the incubated samples have been also provided.

Table 2. 10 The variation of the EC from the incubation and the soil additives as the biochar and the chemical additive ($CaCO_3$) during the incubation duration of 21 days.

Duration (days)	Analyzed parameter	Incubated soil	B 0.5%	B1%	B2.5%	B5%	B10%	C2.5%	C5%	C10%
7	EC (µS/cm)	69.5	148.80	277	393.67	570.33	906.00	160.27	140.70	137.4
14		65.67	140.83	268.0	413.67	596.33	1023.50	126.97	125.67	123.57
21		76.20	126.90	222.33	434.67	699.00	1178.67	164.77	163.77	169.27

Figure 2. 29 demonstrates the alternation caused in the EC of the amended soil with the biochar additive with doses of 0.5% and 1% w/w. As can be observed the enhance in the EC of the soil has been caused with even small doses of biochar (0.5% and 1% w/w) in comparison to the soil as received and incubated soil. Moreover, no noteworthy effect on the EC of the soil was caused during the incubation process.

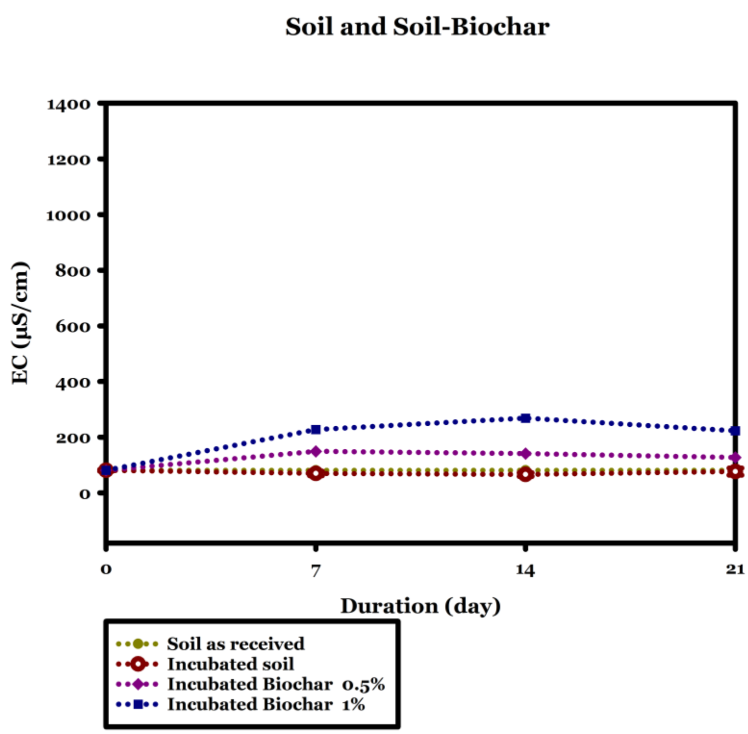

Figure 2. 29 The EC alternation of soil amended with biochar with doses of 0.5% and 1% w/w, produced under certain conditions (from the secondary sludge, with the peak temperature of 450°C and the corresponding rate of 10°C/min) through the incubation test with the duration of 21 days and with 3 replicates for each condition.

Figure 2. 30 illustrates the EC variations caused by biochar additives with doses of 2.5%, 5%, and 10% w/w.

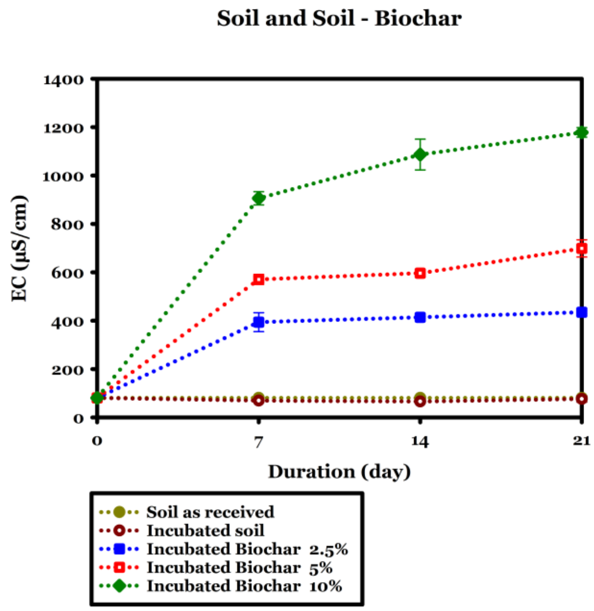

Figure 2. 30 The EC alternation of soil amended with biochar with doses of 2.5%, 5%, and 10% w/w, through the incubation test with the duration of 21 days. The error bars represent the corresponding amount for the replicates (3 replicates) applied for each condition.

Figure 2. 31 represents the EC variations caused by the chemical additive ($CaCO_3$) with doses of 2.5%, 5%, and 10% w/w.

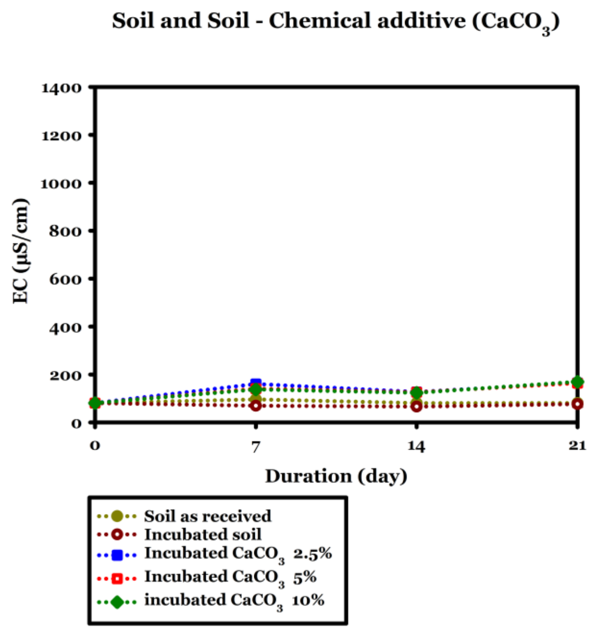

Figure 2. 31 The EC alternation of soil amended with the liming agent containing mainly $CaCO_3$ through the incubation test with a duration of 21 days and with 3 replicates for each condition.

As it can be comprehended from the obtained results in this regard (demonstrated in Table 2. 10, Figure 2. 29, Figure 2. 30, and Figure 2. 31), the biochar additive even in smaller doses improved the EC of the amended soil while with the chemical additive ($CaCO_3$) no enhancement of the EC was obtained in comparison to the soil as received and the incubated soil.

4.2.3. Water holding capacity

During the incubation test, WHC of the incubated conditions was the other parameter that was measured every seven days. Similar to the other measured parameters as pH and EC, the initial WHC of the samples was considered to be the WHC of the soil as received (210.54 g/kg) for day zero. The variations in the WHC of the incubated samples with the biochar (doses of 2.5%, 5%, and 10% w/w) and the liming agent containing mainly $CaCO_3$ (doses of 2.5%, 5%, and 10% w/w) during the incubation period are provided in Table 2. 11.

Table 2. 11 The variation of the WHC from the incubation and the soil additives as the biochar and the chemical additive ($CaCO_3$) during the incubation duration of 21 days.

Duration (days)	Analyzed parameter	Incubated soil	B2.5%	B5%	B10%	C2.5%	C5%	C10%
7	WHC (g/kg)	211.64	257.14	300.56	364.40	184.90	178.32	171.20
14		229.43	256.65	262.53	333.85	223.36	225.27	223.32
21		205.52	234.68	247.09	345.14	213.87	209.66	209.0 5

Moreover, for better visualizations Figure 2. 32 and 2. 33 represent the variation of the WHC in the soil amended with different additives as the produced biochar (with doses of 2.5%, 5%, and 10% w/w) and chemical additive ($CaCO_3$) (with doses of 2.5%, 5%, and 10% w/w).

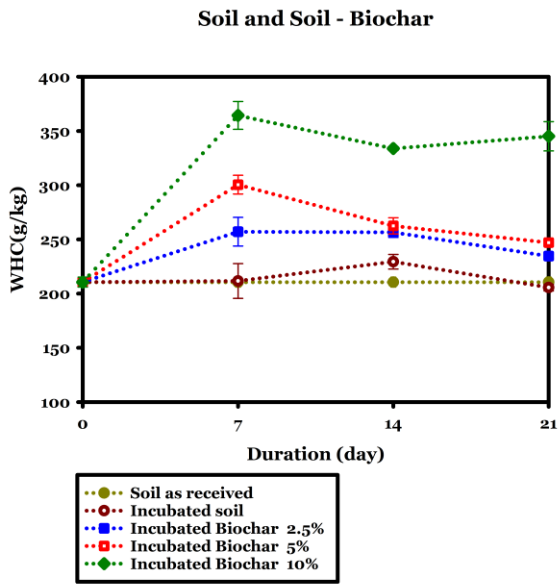

Figure 2. 32 The WHC alternation of soil amended with biochar with doses of 2.5%, 5%, and 10% w/w, through the incubation test with the duration of 21 days. The error bars represent the corresponding amount for the replicates (3 replicates) applied for each condition.

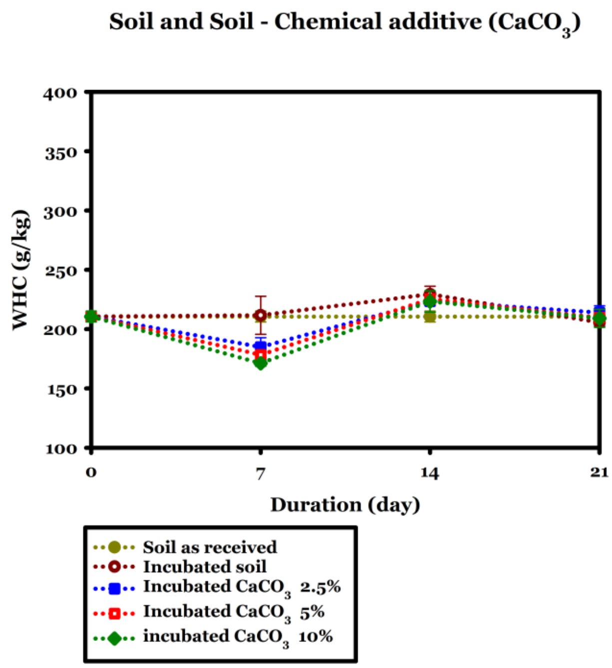

Figure 2. 33 The WHC alternation of soil amended with the chemical additive ($CaCO_3$) through the incubation test with a duration of 21 days. The error bars represent the corresponding amount for the replicates (3 replicates) applied for each condition.

As it can be observed from these figures (Figure 2. 32 and 2. 33), the addition of the biochar as the amendment for the soil, enhanced the WHC of the amended soil via all the doses applied, especially with the dose of 10% w/w (345.14 g/kg). The increase in the WHC of the amended soil with the produced biochar was mainly dependent on the applied dose and as the applied dose was greater this parameter was more significantly enhanced. However, the addition of the chemical additive ($CaCO_3$) caused a decrease on the WHC of the amended and incubated soil samples via the applied doses (2.5%, 5%, and 10% w/w) in the first week of the incubation and at the end of the incubation period (21 days), no notable alternation was caused by this amendment in comparison to the incubated soil and soil as received. In addition, it was observed that the incubation test did not affect the WHC of the soil as no considerable alternation was conducted in the WHC of the incubated soil in comparison to the WHC of the soil as received.

4.2.4. Leaching

The obtained results regarding the leaching capacity of the amended soil with biochar applied in doses of 2.5%, 5%, and 10% w/w in soil via the Mehlich I extraction method and analyzed by the ICP-MS technique regarding the elements as Ca, Na, K, P, Cu, Mg, Ni, Pb, Fe, Zn, Al, and Cr are represented in Table 2. 12. The concentrations of elements as Ni, Cu, and Pb were below the detection limits and they are not presented in this table.

Table 2. 12 The leaching amounts of elements as Ca, Na, K, P, Mg, Fe, Zn, Al, and Cr in the amended and incubated soil with the produced biochar with doses of 2.5%, 5%, and 10% w/w. The symbol "-" in the table represents that the corresponding value was below the measurement detection limit and it was too little to be detectable via this method.

condition	Ca g/kg	Na g/kg	K g/kg	P g/kg	Fe g/kg	Mg g/Kg	Zn g/kg	Al g/kg	Cr g/kg
Soil + Biochar (2.5 % w/w)	1.5656	0.58628	0.148	1.003	0.1611	0.1066	0.006	0.418	-
Soil + Biochar (5 % w/w)	1.9739	0.76593	0.2185	1.273	0.1375	0.1056	0.004	0.506	-
Soil + Biochar (10 % w/w)	4.4206	1.36267	0.502	2.578	0.242	0.2376	0.009	1.012	0.0018

As can be observed from this table, the incubation has enhanced the release of all elements especially Cr as the corresponding value for this element in both the collected soil and the biochar produced (represented in Tables 2.6 and 2.8), were below the detection limit.

4.3. Phyoxicity test

4.3.1. Germination test

Thereafter the duration of 30-34 hours, the incubated samples of the *Lepidium sativum* were analyzed regarding their corresponding G% and L%. Thereafter, the GI% was calculated via the application of Equation 2. 4. Table 2. 13 represents the obtained results regarding the performed analysis. Moreover, Figure 2. 34 demonstrates the variation in the average amount corresponding to the GI% of the 100% dilutions of the incubated samples. As it can be observed from Table 2. 13 and Figure 2. 34, the GI% of the 100% dilutions of the amended soil samples with the produced biochar with different doses (2.5%, 5%, and 10% w/w) were all above 60%, which communicates that the biochar in applied doses does not possess the phytotoxic effects on the germination of the seeds. In addition, by running the one-way ANOVA analysis the corresponding proof value (P=0.599) is greater than the obtained error (set to 0.05). In this condition (dilution of 100%), both the normality test (via Shapito-Wilk) and equal variance test (via Brown-Forsythe) were passed with the corresponding P values of 0.312 and 0.994, respectively. Thus, the hypothesis regarding the equality of the samples is proven and it is safe to state that there is no statically significant difference among the samples. Also, Figures 2. 35 and 2. 36 illustrates the corresponding GI% of the samples in dilutions of 60% and 30%, respectively. The one-way ANOVA analysis performed on the 60% dilution samples also proved that there are no significant differences among the samples (normality test according to the Shapito-Wilk method with P=0.716 and equal variance test according Brown-Forsythe method with P=0.486). However, the one-way ANOVA analysis for the dilutions of 30% represented a significant difference among the samples (according to the Holm-Sidak method with a corresponding P value equal to 0.035 which is smaller than the error of 0.05).

Table 2. 13 The obtained results regarding the phytotoxicity analysis of the extractions of the supplied soil, the incubated soil amended samples with biochar (doses of 2.5%, 5%, and 10% w/w). Three dilutions of 100%, 60%, and 30% were adopted for each condition. In the presented table, the average of three utilized replicates is presented.

condition	dilution (%)	G%	L%	GI (%)
Air-dried and sieved soil	100.0	100.0	103.1	103.1
	60.0	100.0	130.1	130.1
	30.0	92.6	106.1	98.3
Soil + Biochar (2.5 % w/w)	100.0	111.1	90.7	100.8
	60.0	81.5	69.5	56.6
	30.0	96.3	75.6	72.8
Soil + Biochar (5 % w/w)	100.0	100.0	81.2	81.2
	60.0	100.0	78.5	78.5
	30.0	74.1	49.0	36.3
Soil + Biochar (10 % w/w)	100.0	100.0	90.9	90.9
	60.0	88.9	58.6	52.1
	30.0	88.9	57.7	51.3

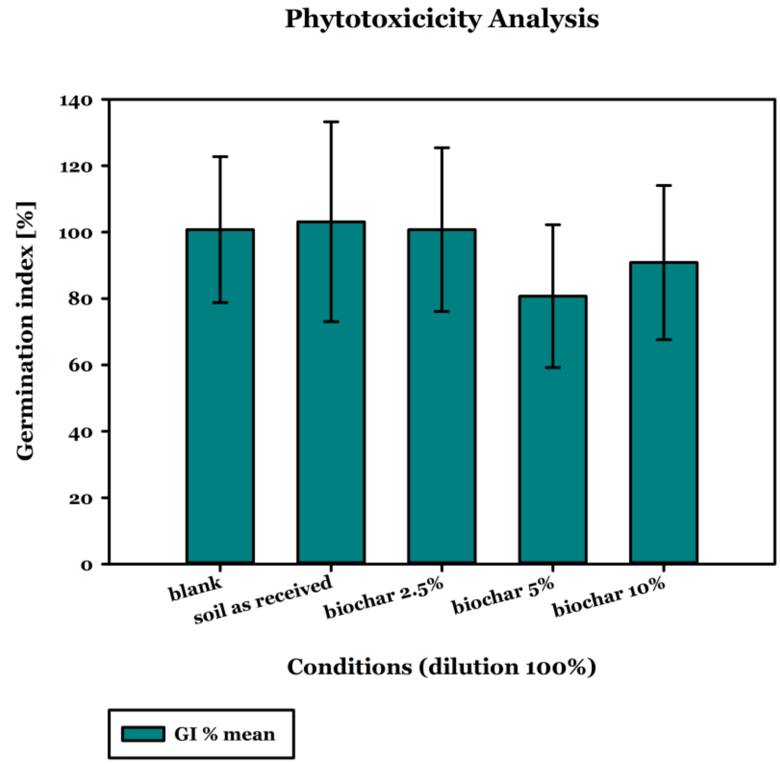

Figure 2. 34 The scheme demonstrating the variation of the GI% of the phytotoxicity of the samples amended with the biochar produced under certain conditions and applied in doses of 2.5%, 5%, and 10% w/w with the dilution of 100%. The error bars illustrate the standard deviation of the three replicates utilized for this analysis.

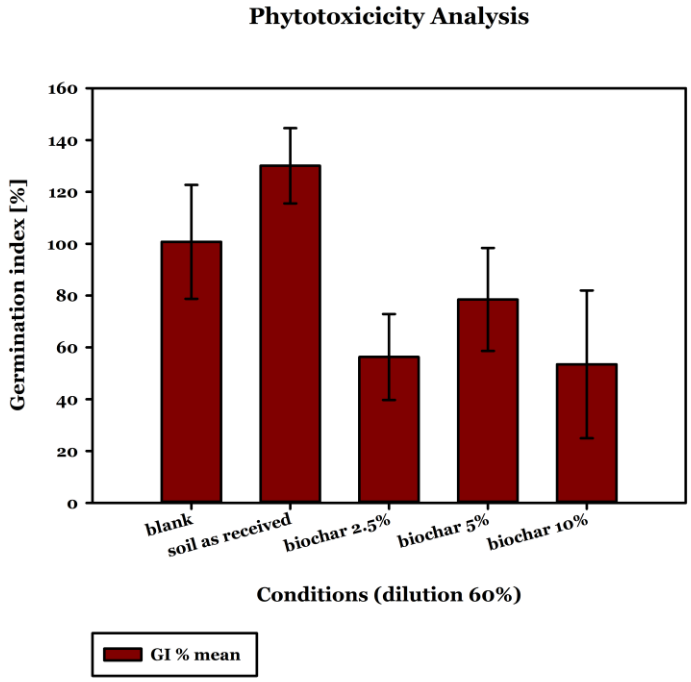

Figure 2. 35 The corresponding GI% of the soil collected and the incubated samples of biochar amended with doses of 2.5%, 5%, and 10% w/w. The dilution of 60% of the extracts has been presented in this figure. The error bars illustrate the standard deviation of the three replicates utilized for this analysis.

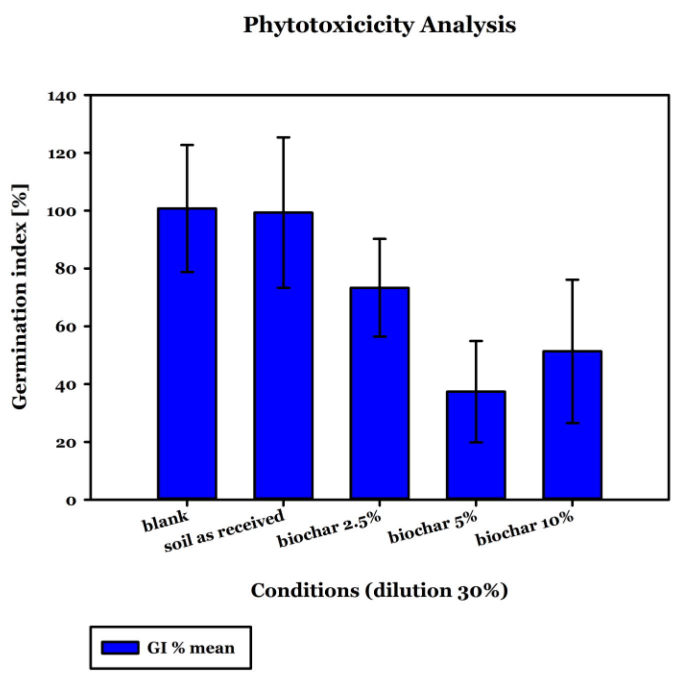

Figure 2. 36 The corresponding GI% of the soil collected and the incubated samples of biochar amended with doses of 2.5%, 5%, and 10% w/w. The dilution of 30% of the extracts has been

presented in this figure. The error bars illustrate the standard deviation of the three replicates utilized for this analysis.

4.4.2. Growth test

4.4.2.1. Germination

The utilized seeds of *Lolium perenne* were tested regarding their health and it was observed that they are approximately 67% fertile as 8 of the 12 seeds germinated in seven days (Figure 2. 13 represents the condition in which the seeds were kept).

Thereafter the plantation of the *Lolium perenne* in the pots with soil (air-dried and sieved by a 2mm sieve), the incubated soil, amended soil with biochar with doses of 2.5%, 5%, and 10% w/w, amended soil with the liming agent containing mainly $CaCO_3$ with doses of 2.5%, 5%, and 10% w/w, and a special condition with the soil (as air-dried and sieved) as the topsoil and the incubated soil amended with biochar of 5% w/w were monitored daily regarding the number of germinated seeds. It was observed that the number of germinated seeds in different conditions varied from one condition to another. The most rapid germination rate was observed in the incubated soil with a duration of 3 days for more than 50% (>10 seeds) of its planted seeds germinated. For conditions as the soil (supplied, air-dried, and sieved), incubated $CaCO_3$ amended soil with doses of 2.5%, 5%, and 10%, and the special adopted condition (air-dried soil as the topsoil and 5% w/w biochar amended soil as the bottom soil) the duration of 4 days was observed to be required for more than 10 seeds to germinate. However, for the incubated biochar amended soil with different doses of 2.5%, 5%, and 10% w/w the durations of 5, 6, and 7 days, respectively, were required for more than 10 planted seeds to germinate. Thus, the germination in the amended soil with biochar took longer in comparison to other conditions.

4.3.2.2. Growth

Although the delay was observed in the amended soil with biochar (2.5%, 5%, and 10% w/w) regarding the duration of the germination of the planted seeds, the growth test was conducted during the 15 days. It was observed that the rate of the growth was rapid in the amended soil with biochar of doses 2.5% and 5% w/w. In these two cases, duplications of the leaves were observed.

3.4.2.3. Yield

The considered parameters for the yield evaluation of the adopted conditions were as the crop height, the dry weight of the crops, the effect of nitrogen addition, and the root development of the plants. The conditions have been ranked according to the corresponding average height of their crops (presented in Table A.1). Moreover, Figure 2. 37 illustrates the crop height in the different adopted conditions as well. As it can be observed from both Table 2. 14 and Figure 2. 37, the amended soil with biochar of 2.5% w/w had the tallest crops (14.51 cm). On the other hand, the amended soil with biochar of 10% w/w and with the addition of N (nitrogen solution) had the shortest crops (5.95 cm). Moreover, the addition of the N did not contribute to the enhancement of the height of the crops.

Table 2. 14 and Figure 2. 38 represent the corresponding dry weight of the crops obtained from the adopted conditions. The condition with the amended soil with 2.5% w/w of the produced was revealed to provide more crops, weight- wise, with the corresponding 0.035g. This amount was calculated to be 77% more crop in comparison to the crops obtained from the condition with the soil (supplied, air-dried, and sieved). While the soil amended with biochar with a dose of 10% w/w was observed to have the least crop, dry weight- wise, with a corresponding dry weight of 0.013g. In comparison to the condition with the soil (supplied, air-dried, and sieved), the approximate 35% reduction in crop yield was obtained in this condition (soil+ biochar of 10% w/w). As it can be communicated from Figure 2. 38, the N addition did not significantly affect the crop dry weight as well. The detailed height of each condition has been represented in Table A.1 in Appendix II.

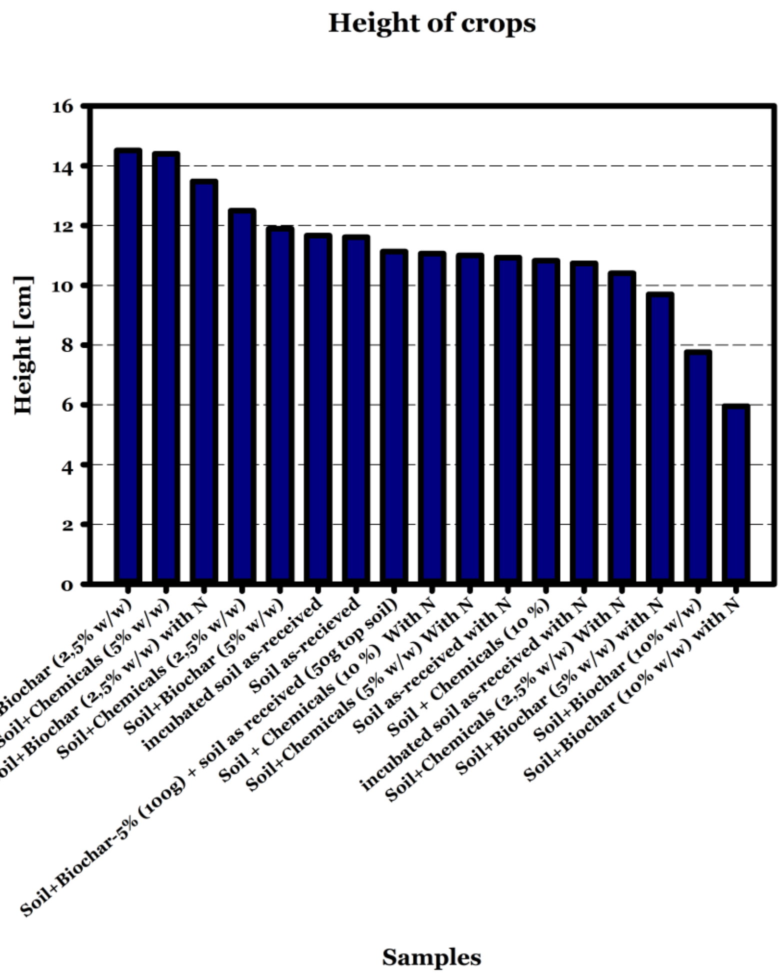

Figure 2. 37 The scheme representing the height of the crops after the conduction of the growth test with a duration of 15 days with *Lolium perenne*. The amended soil with the biochar of 2.5% w/w dose was observed to have the highest crop. The "chemical" stands for the commercial liming agent containing mainly $CaCO_3$ applied as the amendment.

Table 2. 14 The obtained crop dry weight after the conduction of the growth test. The conditions were ranked based on the most crop obtained (weight wise) to the least. Moreover, the variation of the crop dry weight in comparison to the condition of the soil as collected, air-dried, and sieved is also presented.

Samples (ranked based on the dry weight)	Dry weight (g)	Yield variation based on the soil (air-dried and sieved) (%)
Soil+ Biochar (2.5% w/w)	0.035	77
Soil+Biochar-5% (100g) + soil (air-dried and sieved) (50g topsoil)	0.027	38
Soil+ Biochar (5% w/w)	0.026	32
Soil+ $CaCO_3$ (2.5% w/w)	0.021	7
Soil+ $CaCO_3$ (10% w/w)	0.020	3
Incubated soil	0.019	0
Soil (air-dried and sieved)	0.019	0
Soil+ $CaCO_3$ (2.5% w/w)	0.019	-6
Soil+ Biochar (10% w/w)	0.013	-35

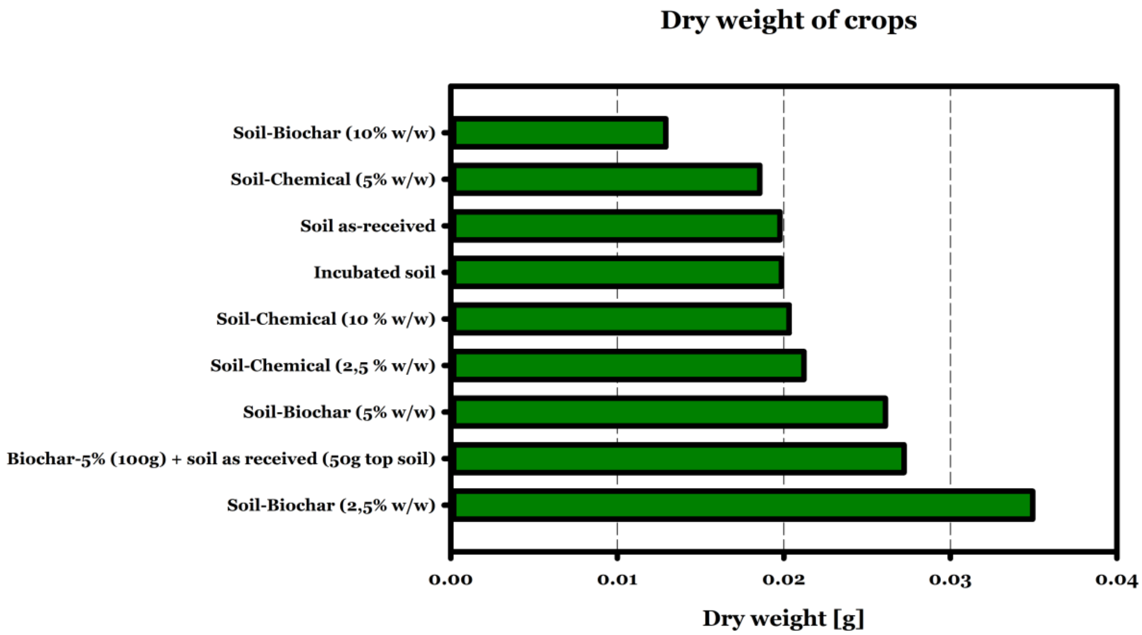

Figure 2. 38 The scheme demonstrating the dry weight of the crops obtained thereafter the conduction of the growth test. The "chemical" stands for the commercial liming agent containing mainly $CaCO_3$ applied as the amendment.

In Figure 2. 39, the development of the roots of the conditions amended with biochar with doses of 2.5%, 5%, and 10% w/w has been presented. The soil amended with biochar with a dose of 2.5% possesses the most developed root (thicker and longer). While the least developed root was observed to correspond to the condition with the soil amended biochar with the dose of 10% w/w.

To sum up, it was observed that the condition with the amended soil with the biochar of 2.5% w/w was the best condition in regards to the crop yield with the highest leaves, the heaviest crops, duplications in leaves, and the most developed roots.

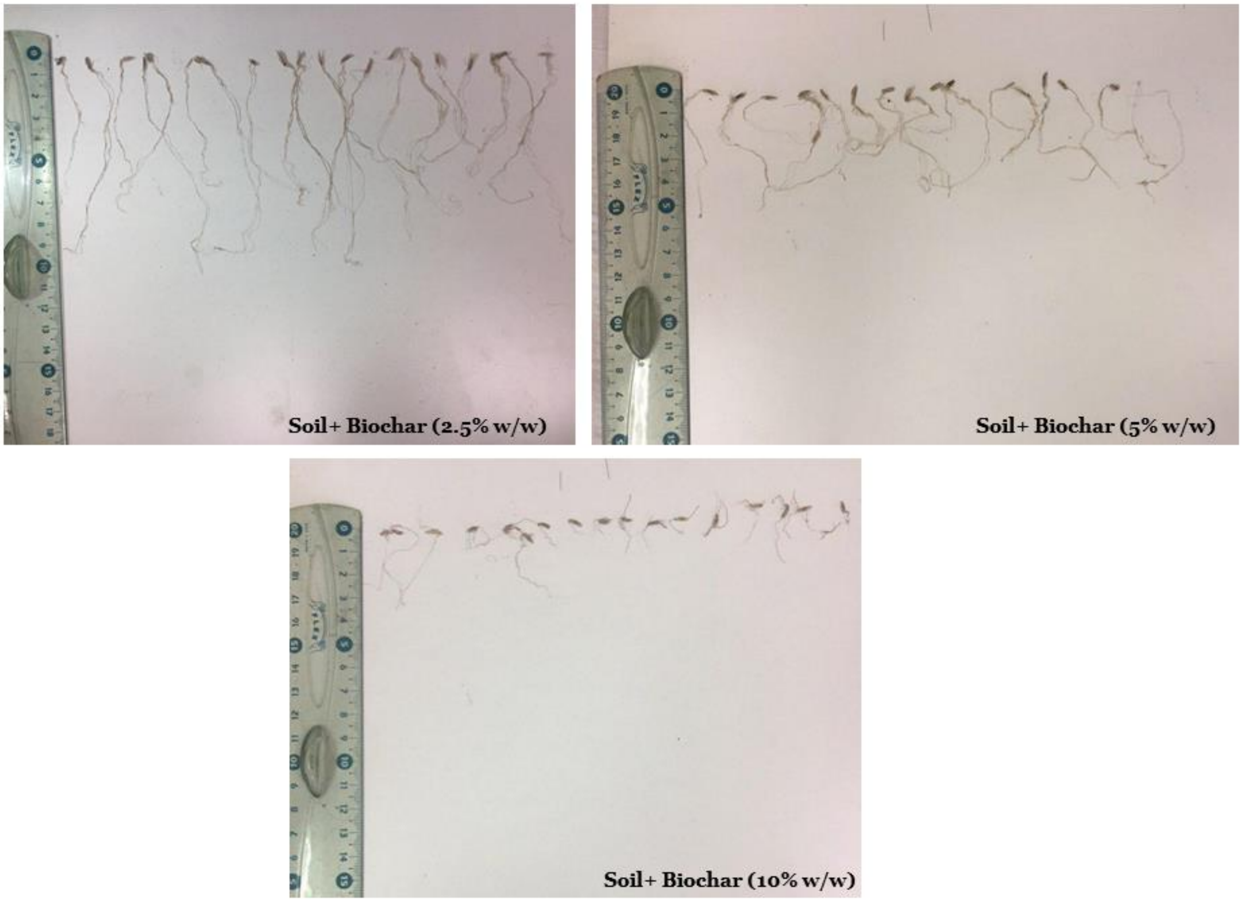

Figure 2. 39 The root developments of the seeds planted into different conditions (soil amended with the biochar of doses as 2.5%, 5%, and 10% w/w). The roots in the soil amended with 2.5% biochar were observed to be the most developed, i.e. it possessed the thickest and longest roots.

5. Discussion

5.1 Biochar, soil, and amended samples characteristics

The obtained results regarding the chemical characteristics of the produced biochar (from the secondary sludge of pulp and paper mill, with 450°C as the maximum temperature, the corresponding rate of 10°C/min, and the residence time of 2 hours) demonstrated that the produced biochar possesses chemical properties semi-similar to other types of biochar pyrolyzed from different types of feedstock and pyrolysis conditions, which have been reported in the literature. Primarily, it was observed that the produced biochar is high in pH. This can be due to the fact that the biochar contains a high amount of $CaCO_3$ (from the XRD analysis with the corresponding rate of 41%), which is accounted as a liming agent itself and normally in the commercial scales, the fertilizers containing this compound are frequently applied for the soil pH correction (Laird *et al.*, 2009). Thus, the application of this product can contribute to lessening the need for fertilizers as a mean of pH adjustment in soils (EUBIA, 2015).

Moreover, the EC of the produced biochar was measured to be high as well. As this biochar is produced from the secondary sludge and sludges normally possess low ash content and high organic matter, the pyrolyzed product produced from this feedstock is accounted to be high in C and ions (Laghari *et al.*, 2016). Consequently, the EC of the sludge-derived biochar is expected to be high as the biochar has the capacity to release various types of ions when extracted and/or applied as a soil amendment (Shah and Shah, 2017). By the performance of the leaching analysis (via Mehlich I extraction method and ICP-MS technique), it was observed that the released ions were mainly Ca, Na, P, and K, which can be accounted as nutrients, and the leaching of heavy metals as Ni, Pb, and Cr are less likely to occur by the application of such amendment as their corresponding concentrations were below the detection limits. Thus, this point can be comprehended that the conversion of the sludge into this biochar has resulted in the immobilization of such toxic elements and there is no concern regarding the bioavailability of such elements for plants in soils amended via this biochar. However, the produced biochar was revealed to be poor in N and as this element is crucial for N cycle in soils, nitrification and consequently plant growth (Nelissen *et al.*, 2015), the application of this biochar alone can not be accounted to sufficiently replace the fertilizers, whether organic and/or inorganic. Furthermore, from the TC analysis, it was comprehended that the produced biochar is indeed rich in C, especially TOC. Thus, the application of the produced biochar in any type of soils can supply C and can be accounted as a semi-permanent C sequestration in soils and, consequently, it can be accounted as a mitigation approach towards the climate change (Muñoz *et al.*, 2017). In addition, the analysis regarding the physical properties of the produced biochar revealed that this biochar has an irregular microstructure, it is highly porous, and its SSA is quite low. These properties are accounted to facilitate the air aeration in soil and also can directly contribute to the enhancement of the WHC of the amended soil (EUBIA, 2015) as the water droplets can be captured in the pores of the biochar (Rasa *et al.*, 2018). The increase in the aeration can directly improve the root development of plants and promotes the absorption of the nutrients which both can result in better crop yield from a quantitative point of view (Wilujeng and Handayanto, 2019). Moreover, the enhancement of the soil WHC directly contributes to the water provision for the plant uptake and better water adsorption by plants through the irrigation cycles and/or precipitation (Rasa *et al.*, 2018; Safaei Khorram *et al.*, 2019). Also, the increase in the WHC of the soil can become advantageous in the case of the drought as it provides water storage in the soil for plants and it can reduce the salt stress on them (Ali *et al.*, 2017).

Despite all, this point should not be neglected that the sludge utilized as the feedstock for this biochar production is waste produced from the treatment of pulp and paper mill wastewater, which is accounted as one of the most toxic types of industrial wastewaters (Ali and Sreekrishnan, 2001). Such waste is quite large in quantity and due to lack of available land and also fulfilling the stringent regulations corresponding to the prevention of soil and water contamination, the landfilling of the sludge is no longer an option. Previously, the sludge was accounted as a nuisance, however, currently, it has been redefined as a resource (Raheem *et al.*, 2018). The conversion of sludge into biochar through a pyrolysis process has been accounted for as a suitable means of management of such a waste and has highlighted its hidden potential as a soil amendment. Also, the application of such biochar produced from the biological sludge does not interfere with the food industry over the provision of the initial feedstock. However, the need for conduction of more research is still greatly felt in order to facilitate the safe application of such sludge-derived biochar in soils.

For the purpose of this study, the soil supplied by the pulp and paper industry and collected from its forest soils, was also analyzed regarding its properties. The obtained results in this regard demonstrated that the soil is accounted to be acidic and its corresponding value regarding its WHC and EC were measured to be quite low. Moreover, according to the results achieved via the SEM and EDX analysis, it was observed that the soil has an irregular microstructure and it is low in the elements such as P and N considered necessary for plant growth (Vaccari *et al.*, 2015), i.e. the collected soil can be accounted to be low in fertility. Thus, the collected soil can be accounted to be suitable to put the potential of the produced biochar into an assessment regarding its capacity to alter and improve the properties of the soil from the fertility point of view. Moreover, the application of the biochar produced from the biological sludge from the wastewater treatment of a pulp and paper industry and its application on the forest soil of the same industry can facilitate not only the waste management of such an industry but also provides a sustainable aspect in the industry by the elimination of the CO_2 released in accordance with a climate change mitigation methods and also by sequestration of C in its soil (Passarini *et al.*, 2014).

However, the immediate alternation in the properties of the amended soil is not sought and the question remains regarding the long-term effects of the addition of such biochar in the soil as an amending additive. Thus, an incubation test was implemented to evaluate the long-term effects of the produced additive in the soil (Luo *et al.*, 2016). During the incubation period (21 days), the alternations caused by the biochar additive in different doses on three parameters as pH, EC, and WHC were measured on a weekly basis. Also, to facilitate the comprehension of the obtained results, an incubation test on the soil amended with a commercial liming agent containing mainly $CaCO_3$ occurred simultaneously. The obtained results proved that the addition of the biochar even in small doses as 0.5% and 1% w/w possess the capacity to neutralize the pH of the collected acidic soil (with the corresponding pH of 4.9). However, in order to obtain a fertile soil, the alkalinity is a crucial factor and the addition of the liming agent even in the smaller dose as 2.5% w/w enhanced the pH of the soil considerably. Thus, it can be concluded that for the higher pH, higher doses of biochar are required which raises the question regarding the phytotoxicity of the application of the biochar.

5.2 phytotoxicity assessment

Thereafter the incubation period, a leaching test was performed on the incubated amended samples with biochar of doses as 2.5%, 5%, and 10% w/w via the extraction method of Mehlich I and ICP-MS analysis. Despite the fact that no concentration of Cr was observed in the soil (as supplied, air-dried, and sieved) and the produced biochar, the small concentration of Cr as 0.0018 g Cr/kg of amended soil with 10% w/w of produced biochar was observed. As expressed in the Portuguese decree-law of n.º 103/2015 (Manuela *et al.*, 2004), the acceptable concentration of Cr in the commercial fertilizer present in the market must not exceed 100 ppm (0.1 g Cr/kg). Thus, it can be observed that the concentration of the Cr in the amended soil with the biochar is less than the mentioned concentration in the decree-law. Also, as previously mentioned, the corresponding limit of Cr in both the soil and the biochar was below the detection limits and the corresponding concentration is neglectable. This point can be comprehended that the incubation may have resulted in the release of this element and the adopted extraction method (Mehlich I) was not acidic enough to facilitate the release of this element in the produced biochar. Moreover, as no concentration of the Cr was not observed in the soil itself and also in the amended samples with biochar doses of 2.5% and 5% w/w, it can be assumed that the corresponding concentration of Cr was caused by the biochar itself and the incubation has facilitated its release in the bigger applied dose as 10% w/w.

However, this point should not be neglected that no corresponding values regarding the concentrations of Zn, Ni, and Pb were observed in any of the samples. Thus, it can be concluded that the conversion of the secondary sludge into biochar has caused the immobilization of such elements which are presented in high concentrations in such a sludge (Méndez *et al.*, 2012).

In addition, thereafter the incubation period (21 days), it was observed that the color of incubated samples with biochar additives in doses of 2.5%, 5%, and 10% have darkened in comparison to the soil as collected and also the incubated soil. Thus, it can be concluded that the biochar additive possesses the capacity to darken the soil color. This point is of high significance due to the direct relation of the soil color with the albedo, aka reflectivity, of the soil without any plantation (Post *et al.*, 2000). In order for the application of the biochar to be accounted as a climate change mitigation, the albedo of the amended soil should be taken into consideration as the heat of the solar radiation can be imprisoned in the soil during the daytime and varies the soil temperature and the moisture content of the amended soil (Usowicz *et al.*, 2016).

Further on, via the application of the biochar, it was observed that aside from the pH of the soil other aspects as the EC and the WHC have both enhanced significantly in comparison to the soil as collected, incubated soil, and amended soil with the commercial liming agent containing mainly $CaCO_3$ (with doses of 2.5%, 5%, and 10% w/w). To assess the effects of these alternations on the soil fertility, a germination test and a growth test were proceeded. From the execution of the germination test via the application of *Lepidium sativum*, it was observed that the mean value of the GI% of the samples amended with biochar of doses 2.5%, 5%, and 10% in the 100% dilutions were all above 60% demonstrating the non-toxic effect of the biochar additive on the seed germination. Moreover, the results achieved thereafter the execution of the growth test implied that the application of the biochar with the dose of 2.5% without the addition of the N solution has enhanced the crop yield to 77% in comparison to the soil (supplied, air-dried, and sieved). While the application of the biochar in the dose of 10% w/w resulted in the reduction of the crop yield to -35% in comparison to the crop yield obtained from the soil (collected, air-dried, and sieved). Thus, this point can be concluded that the application of the biochar, the biological sludge from the wastewater treatment of a pulp and paper industry, in small doses as 2.5% w/w can be a suitable replacement of the commercial fertilizer, whether organic and inorganic, to enhance the soil fertility and consequently increase the crop yield. In addition, it was observed that the plants which had grown in the amended soil with biochar of 2.5% w/w dose had developed longer and stronger in comparison to the roots developed in the soil amended with biochar of doses of 5% and 10% w/w (demonstrated in Figure 49). The better development of the roots in the soil amended with biochar of 2.5% w/w dose can be related to the reduction it had caused in the soil tensile strength and also the facilitation of air aeration due to the biochar pores (Lehmann *et al.*, 2011). However, as the root development in the conditions with biochar doses of 5% and 10% w/w was quite insignificant, it can be concluded that the presence of toxic compounds and elements may have hindered the root growth and development. Thus, more research is still accounted to be essential to evaluate the effects of the biochar addition in various doses such as research regarding the plant uptake (Mohawesh *et al.*, 2018), the corresponding concentrations of heavy metals bioavailability, heavy metal absorption by plants (Liu *et al.*, 2018), the soil respiration (Singh and Mavi, 2018), and the soil microbial community (Duan *et al.*, 2018).

6. Conclusion

In this study, the biochar produced from the biological sludge from the wastewater treatment of a pulp and paper industry, under pyrolysis condition of 450°C as the maximum temperature, with a corresponding rate of 10°C/ min, and the residence time of two hours was evaluated regarding its properties. It was observed that the produced biochar possesses high pH and EC. Moreover, it was revealed that this biochar has an irregular microstructure and it is highly porous. Thereafter the evaluation of the characteristics of the produced biochar, it was applied in the soil collected from the industrial site of the same mill. In order to assess the long-term effects of the biochar as a soil amendment, an incubation test was conducted with additive doses of 0.5%, 1%, 2.5%, 5%, and 10% w/w. In addition, to provide a comparison, a commercial liming agent containing mainly $CaCO_3$ was also applied as different samples with the doses of the 2.5%, 5%, and 10% w/w. Every seven days, the properties as the pH, EC, and the WHC of the samples were measured. Thereafter 21 days, these characteristics reached semi-stability, and then the incubation was stopped, and this duration was considered as the incubation duration. During this period, it was observed that the biochar has the capacity to enhance the pH, EC, and WHC of the soil simultaneously, while the liming agent just enhanced the pH of the soil significantly and no considerable variation was observed regarding the EC and the WHC of the samples amended with the liming agent. Further on, the leaching test was conducted on the incubated samples amended with biochar additive doses of 2.5%, 5%, and 10% w/w via the Mehlich I extraction method and analysis of ICP-MS. It was observed that the concentrations of the heavy metals as Ni, Pb, and Zn were below the detection limit. However, a small concentration of Cr was observed in the incubated samples with biochar of 10% w/w. While the concentration corresponding to Cr was less than the acceptable amount of fertilizers in the market according to the Portuguese decree-law and no exceedance was observed. Moreover, the phytotoxicity analysis containing a germination test via *Lepidium sativum* and a growth test with *Lolium perenne* were conducted. The obtained results regarding the germination test indicated that no toxic effect was observed in the 100% dilution of the incubated samples with biochar with doses of 2.5%, 5%, and 10% w/w as the corresponding GI% for all the samples were above 60%. Also, the results achieved from the growth test showed a 77% increase in the crop yield in the amended soil with biochar of dose 2.5% w/w (more dry weight and higher crops). However, a negative effect as -35% on the crop yield was observed from the amended samples with biochar doses of 10% w/w. Also, well-developed roots were observed in the amended soil with biochar dose of 2.5% while the roots in the soil amended with the biochar of doses as 5% and 10% w/w were poorly developed. In addition, no considerable variation in the crop yield was observed with the addition of the liming agent and also in the pots irrigated with N solution. Thus, this point can be concluded that the application of this biochar (from the biological sludge from the wastewater treatment of a pulp and paper industry and under the previously mentioned pyrolysis condition) can be accounted as a suitable replacement of the commercial correctives, whether organic and inorganic, as it enhanced the soil fertility and consequently the crop yield if only applied in small dose as 2.5% w/w. Also, due to the high C content of the produced biochar, it can be utilized as a C storage in soils and also as a climate change mitigation approach due to the fact that it can replace the fertilizer and consequently the greenhouse gases produced from the agricultural activities will be minimized. In addition, the application of this biochar can be accounted for to be sustainable waste management and, consequently, it is in compliance with sustainable development goals. However, more research regarding the other aspects such as the bioavailability of heavy metals, plant uptake, soil respiration, soil microbial community, etc. is still accounted to be essential to a safe application of such biochar.

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Appendix I

This section has been prepared in order to demonstrate the figures inserted in the chapter one of this thesis with the actual centralities obtained from the utilization of CiteSpace application.

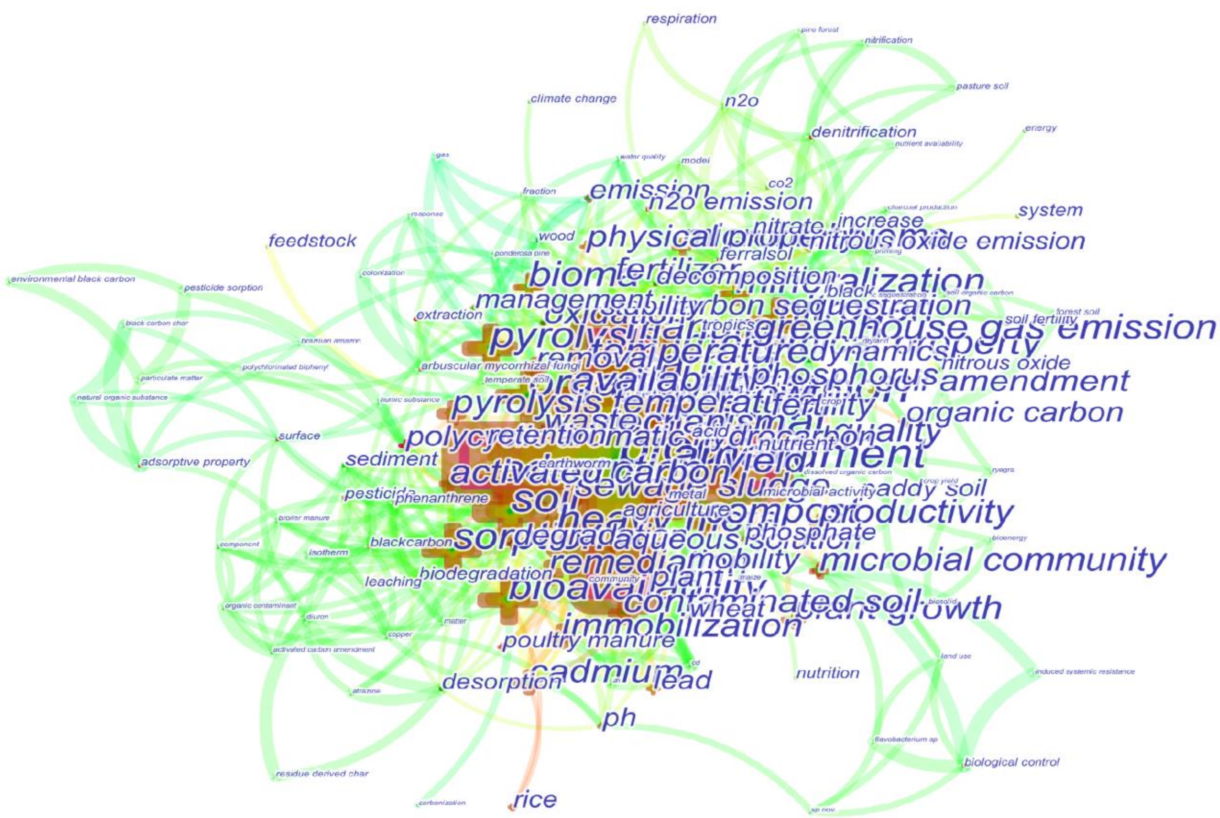

Figure A. 1 A schematic representation of co-occurring analysis of the keywords appeared in the scientific documents published on the application of biochar for soil treatment with actual centrality.

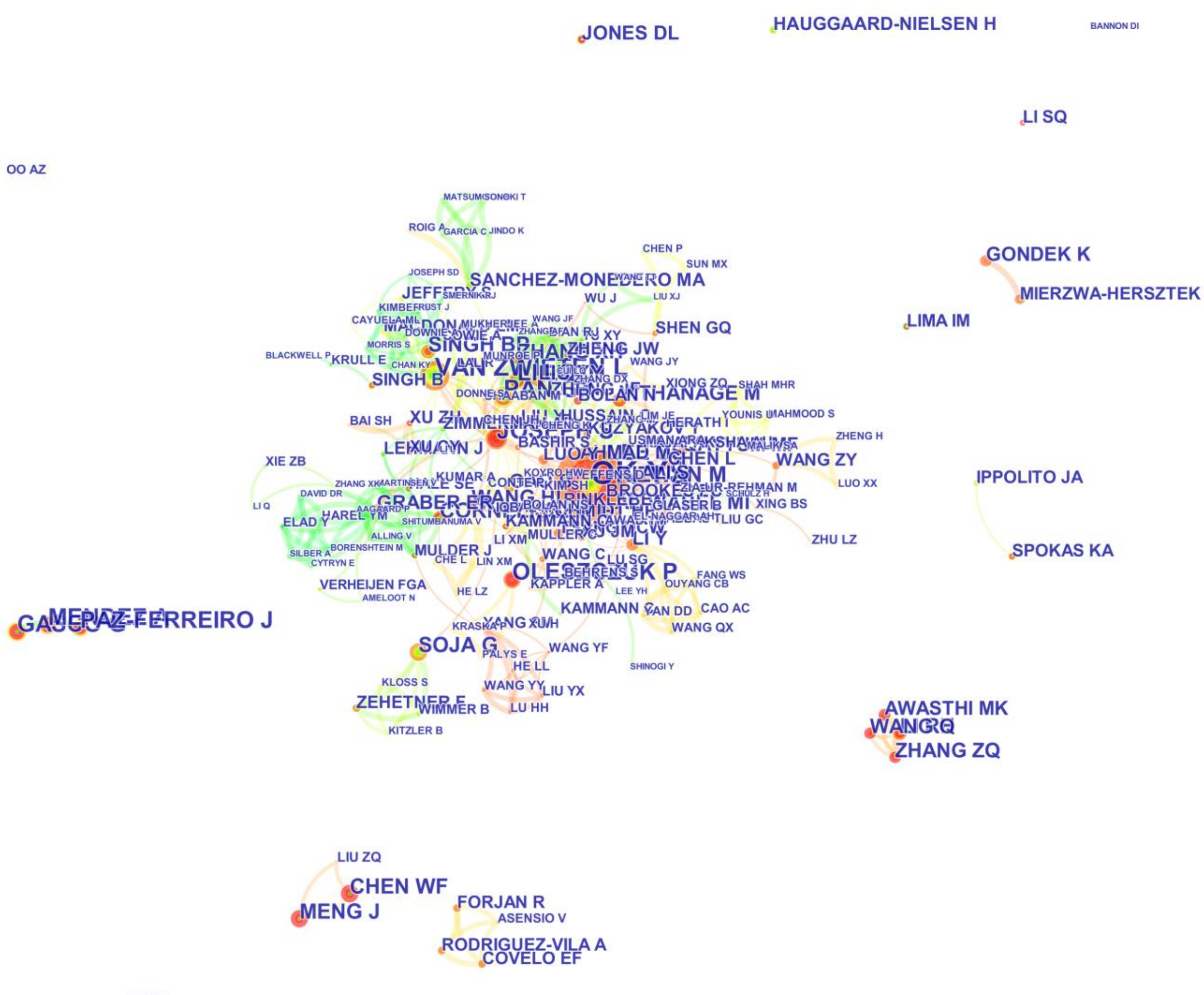

Figure A. 2 A schematic to illustrate the authors contributed in scientific publications on the application of biochar for soil amendment with actual centrality.

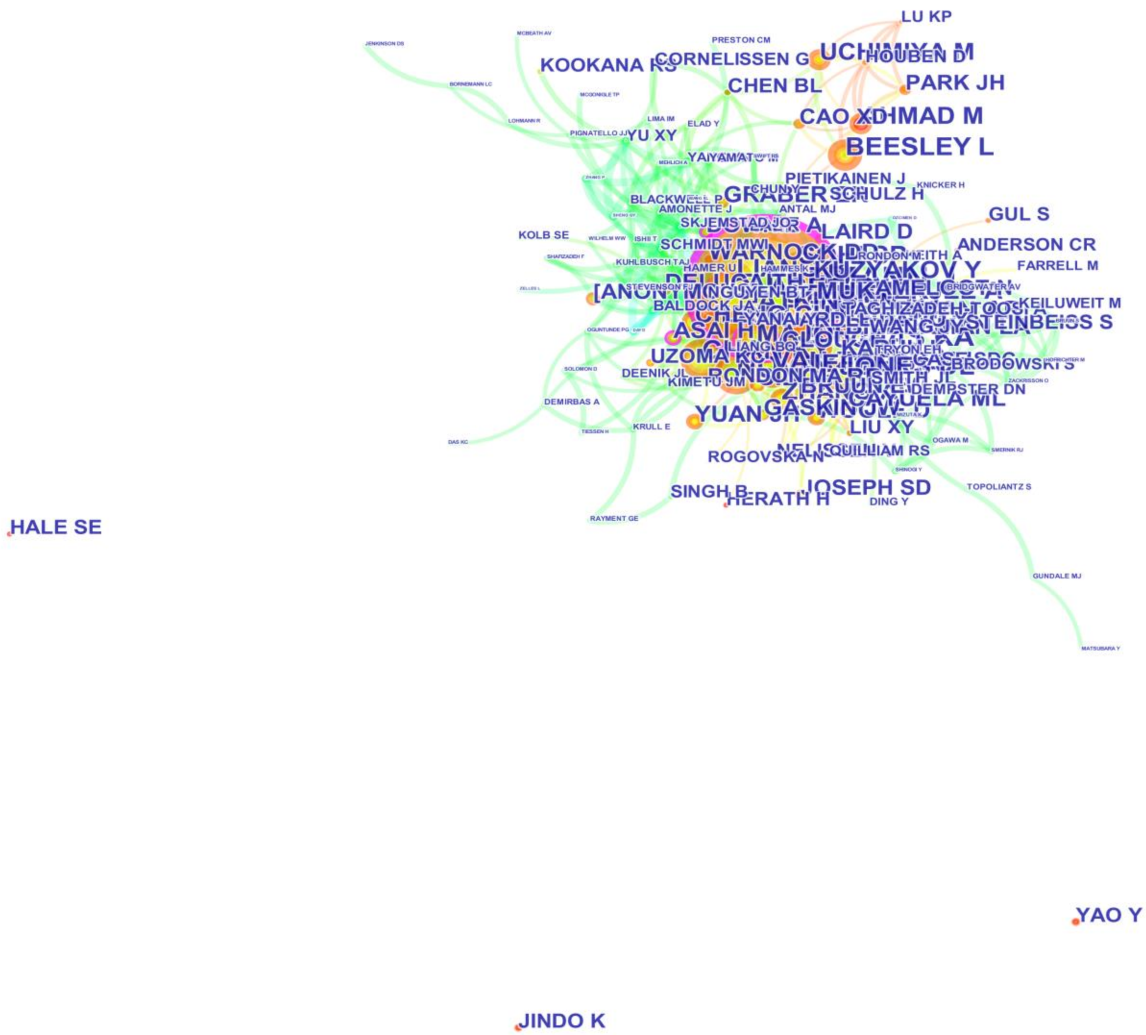

Figure A. 3 A schematic illustration demonstrating the most cited authors publishing scientific documents on the biochar application for the soil amendment with actual centrality.

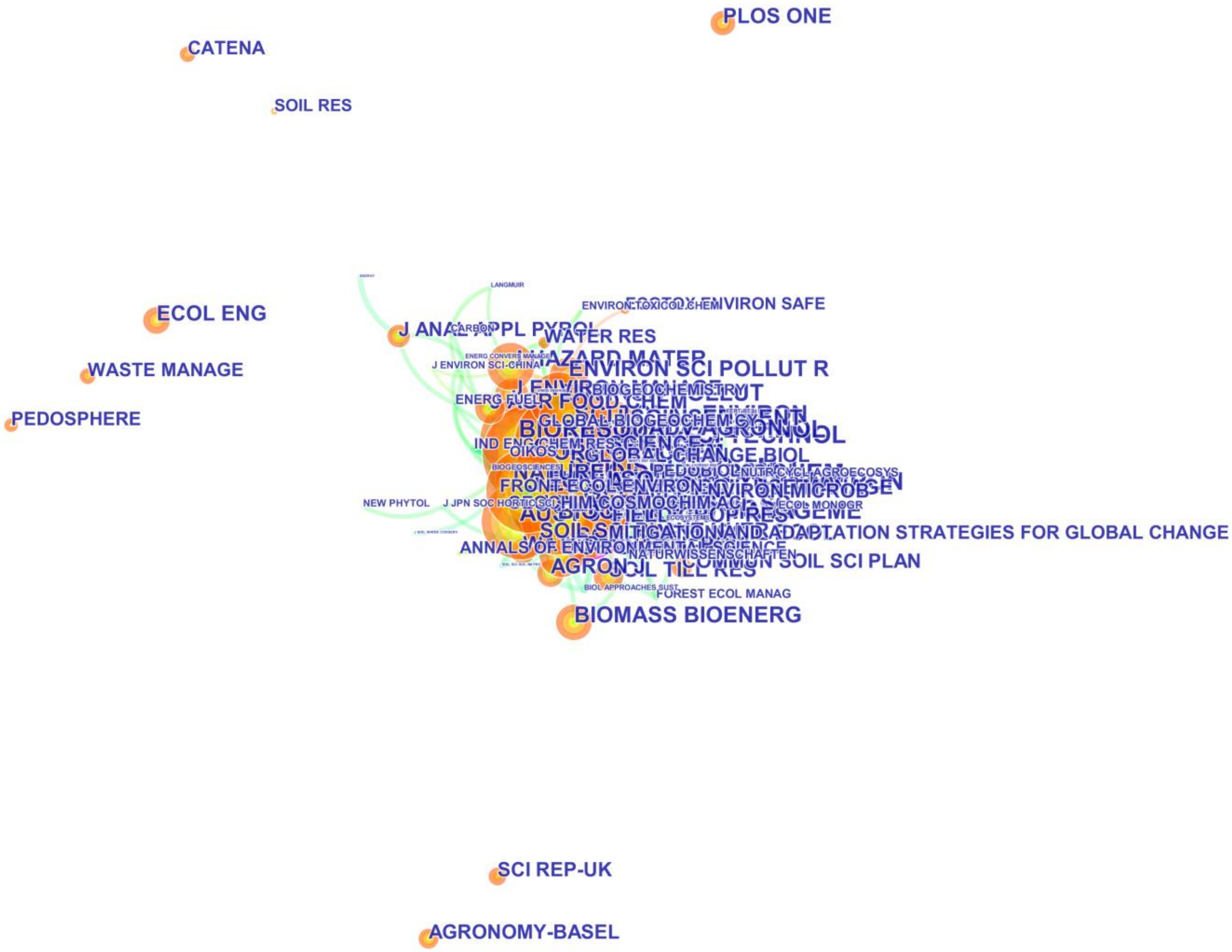

Figure A. 4 The cited journals analysis with minimum overlap obtained from CiteSpace.

Appendix II

The results regarding the exact height of the leaves grown in the adopted conditions (the soil as received, incubated soil, amended soil with biochar with the doses of 2.5%, 5%, and 10% w/w, the amended soil with chemical additive with the corresponding doses of 2.5%, 5%, and 10% w/w, and the special condition with the soil as received as the topsoil and the biochar amended soil of 5% w/w as the bottom soil) individually and also with the effect of N solution irrigation, are represented in Table A.1.

Table A.1 The adopted conditions for the growth test have been ranked according to the corresponding average height of their crops. This measurement was conducted via the application of a ruler with the corresponding accuracy of mm.

Samples (ranked based on the height)	Height (cm)
Soil+ Biochar (2.5% w/w)	14.51
Soil+ $CaCO_3$ (5% w/w)	14.40
Soil+ Biochar (2.5% w/w) with N	13.48
Soil+ $CaCO_3$ (2.5% w/w)	12.50
Soil+ Biochar (5% w/w)	11.9
incubated soil	11.67
Soil (air-dried and sieved)	11.61
Soil+Biochar-5% (100g) + soil (air-dried and sieved) (50g topsoil)	11.13
Soil + $CaCO_3$ (10 %) with N	11.06
Soil + $CaCO_3$ (5% w/w) with N	11.00
Soil (air-dried and sieved) with N	10.93
Soil + $CaCO_3$ (10 %)	10.82
incubated soil with N	10.74
Soil + $CaCO_3$ (2.5% w/w) with N	10.40
Soil+ Biochar (5% w/w) with N	9.70
Soil+ Biochar (10% w/w)	7.76
Soil+ Biochar (10% w/w) with N	5.95