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Effects of Using Softwood Pellet Biochar Prepared at Different Temperatures with Grass Chippings on Retention of Heavy Metals in Contaminated Soils

Kyari Umar Dunoma[1], Limin Ma[1,2*], Xingquan Shu[1], Haiyan Yu[1], Weiwei Zhang[1], Chengcheng Bu[1], Yong-Sik Wang[1], Jiahong Luo[1], Guangyao Chen[1], Jinpeng Yu[1], Ru Zhang[1], Yuchen Han[1], Haoyu Zeng[1], Matthew S. Wisseh[1], Amina Grema Mustafa[3], Mohammad Auwal Saidu[3], Mufidat Mamman Khan[3]

[1]College of Environmental Science and Engineering, Tongji University, Shanghai, China
[2]Key Laboratory of Yangtze River Water Environment, Ministry of Education, Tongji University, Shanghai, China
[3]Environmental Assessment Department, Federal Ministry of Environment, Abuja, Nigeria
Email: *lmma@tongji.edu.cn

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Abstract

Heavy metals have been viewed as hazardous environmental pollutants, and anthropogenic activities due to their high toxicity and persistent nature in the environment. Anthropogenic activities such as artisanal mining, industrial activities, improper usage of fertilizers and pesticides, and indiscriminate open waste disposal bring about an increase in the presence of heavy metals in the environment. In the Keffi Metropolis, different elements lead to land contamination which debilitates soil quality, plant survival, human well-being, and the environment as a result of extensive dispersion or quantity of heavy metals in the soil and water. In recent years, biochar has emerged as a promising soil amendment for mitigating heavy metal pollution due to its unique physicochemical properties. This paper provides the effects of softwood pellet biochar on the retention of heavy metals in contaminated soils. A microcosm experiment was carried out to investigate the effects of biochar on the retention of heavy metals in contaminated soils. This research aimed to give an overview of the effects of softwood biochar at different temperatures (550˚C and 700˚C) on the retention of heavy metals and metalloids released from the soil during water inundation. The results show that the addition of organic matter (grass chippings) minimizes heavy metal mobilization. Also, biochar at high temperatures is more effective than those at low temperatures. The expected outcome of the research analysis includes providing insights into the role of biochar in retaining heavy metal contamination and further under-

standing the use of biochar as a sorbent for the management of contaminated soil.

Keywords

Softwood Biochar, Heavy Metal, Contaminated Soil, Grass Chips, Keffi Metropolis, Microcosm

1. Introduction

Heavy metal contamination of soils is a pervasive environmental problem, impacting agricultural productivity, ecosystem health, and human well-being. Sources of heavy metal pollution include industrial discharges, mining activities, improper waste disposal, and the widespread use of fertilizers and pesticides. These heavy metals, such as lead (Pb), cadmium (Cd), chromium (Cr), and arsenic (As), are highly toxic and can persist in the environment, posing long-term risks due to their non-biodegradable nature and potential for bioaccumulation in the food chain. Heavy metals are metallic elements having relatively high density (5.0 g/cm^{-3}) and might be toxic at lower concentrations. However, another definition of heavy metals states that it is a metallic chemical element having a relatively high atomic number and occurs naturally in soils and rocks via human activities which causes an increase in the metal concentration [1] [2]. Industrialization and human activities have led to an increase in the level of metal concentrations. Unlike organic contaminants, heavy metals are natural constituents of the earth's crust and stay in the environment because they cannot be destroyed or degraded and tend to bioaccumulate [2] [3]. Anthropogenic activities such as smelting, mining, waste disposition, combustion of fossil fuel, and chemical and manufacturing activities have led to an increased level of heavy metals in the environment [4] [5]. Heavy metals have been viewed as hazardous chemicals that pollute the environment due to their toxic nature even at lower concentrations. Heavy metals that are most commonly found at contaminated sites include arsenic (As), cadmium (Cd), chromium (Cr), mercury (Hg), Lead (Pb), which are non-essential, and copper (Cu), nickel (Ni), zinc (Zn), which are essential and may lead to health problems in humans [6]-[9]. These metals are highly toxic even in low quantities and the increased quantity of heavy metals due to emissions from industrial activities is of major concern as most of these metals are discharged into freshwater without sufficient treatment [10] [11]. Heavy metals have a long-term persistence in soil because they do not undergo chemical or biological degradation which makes soil the major sink for heavy metals release [12] [13]. Heavy metals stand out from other elements because of their high toxicity, bio-accumulative nature, and bio-magnification. The ability of heavy metals to bio-magnify and bio-accumulate could have long-term health effects on humans and their environments [14]-[16].

Heavy metals in soil systems originate from many sources. However, the ma-

jor sources have been identified as naturally occurring in the soil and human anthropogenic activities such as smelting of ores, waste incinerators, mining, coal combustion, fossil fuel combustion, industrial wastewater, sewage sludge or municipal compost, pesticides, and fertilizers [10] [17]. All these activities harm the quality of the soil which thereby affects soil properties like the chemical and physical elements in the soil [9] [18] [19].

As stated by [18] [20], due to industrialization, heavy metals and metalloids accumulate in the soil through emission from human activities and anthropogenic sources thereby affecting the soil quality conditions such as the soil pH, nutrients, moisture content, and humus content [21]. Several studies explained that heavy metal concentration in soil stays for a long time as it does not undergo microbial or chemical degradation but is bioavailable and changes are seen in their chemical form [3] [13] [22]. Biodegradation of organic contaminants hinders the presence of toxic metals in the soil. Heavy metal contamination poses a major problem to humans and the environment. The risks and hazards of heavy metals are great as they could contribute to global warming and may lead to serious health problems [23] [24]. A major entry pathway of heavy metals contamination into the human body is directly or indirectly through the food chain (soil-plant-human or soilplant-animal human), drinking of contaminated groundwater, reduction in food quality (safety and marketability) via phyto-toxicity, reduction in land usability for agricultural production causing food insecurity [2] [13] [25]-[27]. Soil contamination by heavy metals requires remediation as appropriate restoration methods of soil amendments are being developed [14] [28]. Furthermore, the increased shift from traditional techniques to greener and cheaper alternatives of soil remediation is frequently looked into; for instance, heavy metal transfer to groundwater and soil ecosystem can be reduced by situ metal stabilization [29], the food chain toxicity and accumulation can be reduced by bioavailability, biochar can be used for immobilization of contaminated soil and water [5] [30]. Biochar, a carbon-rich material produced from the pyrolysis of organic matter under limited oxygen conditions, has emerged as a promising solution for soil remediation. Biochar's porous structure, large surface area, and functional groups can enhance its capacity to adsorb and immobilize heavy metals, thereby reducing their bioavailability and toxicity. However, the effectiveness of biochar in retaining heavy metals depends significantly on the feedstock used and the conditions under which it is produced, particularly the pyrolysis temperature [31]-[34]. Softwood pellets, as a biochar feedstock, offer several advantages, including uniformity, high carbon content, and ease of handling. Additionally, the incorporation of grass chippings, an abundant and renewable organic resource, can potentially improve the nutrient profile and enhance the overall effectiveness of the biochar-soil amendment. This study focuses on investigating how the pyrolysis temperature of softwood pellet biochar, when used in combination with grass chippings, affects the retention of heavy metals in contaminated soils [34]-[37]. Despite the promising po-

tential of biochar for soil remediation, several questions remain unanswered, how does pyrolysis temperature influence the physicochemical properties of softwood pellet biochar? What is the optimal pyrolysis temperature for maximizing heavy metal retention in contaminated soils? How do grass chippings interact with softwood pellet biochar to affect heavy metal immobilization? What are the long-term impacts of biochar and grass chippings on soil health and heavy metal dynamics? Addressing these questions is crucial for developing effective biochar-based soil remediation strategies and understanding the underlying mechanisms that govern heavy metal retention in soil. Numerous studies have explored using biochar for heavy metal immobilization in soils. Studies have shown that higher pyrolysis temperatures generally increase biochar's surface area and pore volume, enhancing its adsorptive capacity for heavy metals. For instance, [33] [36] reported that biochars produced at higher temperatures effectively immobilized Pb and Cd in contaminated soils. [38]-[40] highlighted that biochars derived from different feedstocks, such as wood, crop residues, and manure, have varying capabilities in heavy metal retention. The type of feedstock used for biochar production significantly affects its properties and performance. [33] [37] demonstrated that the addition of organic matter, such as compost or manure, alongside biochar, could enhance nutrient availability and improve heavy metal immobilization in soils. This study differs from the previous studies as it aims to provide a detailed understanding of how pyrolysis temperature affects biochar properties and their efficacy in heavy metal retention. The novel aspect of combining softwood pellet biochar with grass chippings is explored to evaluate the potential synergistic effects on heavy metal immobilization and soil health. This study not only focuses on the immediate impacts of biochar and grass chippings on heavy metal retention but also considers the long-term implications for soil health, providing a holistic view of biochar application in contaminated soils.

2. Materials and Methods

2.1. Soil and Biochar Samples Used in the Experiment

Soil samples were collected at different waste dumpsites within the study area at a depth of 0 - 30 cm in the Keffi Metropolis, Nasarawa State, Nigeria, and Softwood Pellet biochar (SWP) sample was bought from Lamar Kanadi Manure and Biochar, Dandal Kura Road, Abuja, Nigeria. Samples were heated at 45˚C and air dried for 48 hours, grounded and sieved to 2 mm and 63 μm, to achieve a homogenous size and stored in smaller labeled bags before analysis, similar to a process conducted by [41].

2.2. Equipment, Apparatus, and Chemical Reagents

The equipment and apparatus used for this project are Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), pH meter, weighing balance, beakers, mortar and pestle, X-ray Fluorescence (XRF) analyzer, fume cupboard,

Dissolved Oxygen meter (DO), syringes, 0.22 μm syringe filter, centrifuge tube, digestion bottles, oven, stainless steel sieve, microwave digester and mechanical shaker. The reagents and chemicals used during this experiment are analytically graded including Nitric acid (HNO_3), Acetone, Ultra-pure water (18.2MX cm), and distilled water.

2.3. Methods for Characterization of Soil and Biochar Samples

2.3.1. pH and Electric Conductivity (EC)

A sample of soil at a 1:50 ratio was measured (soil:water), 1 gram of biochar was added; 50 ml of Ultra-pure water (18.2MX cm) was added and then placed in a shaker for an hour at 150RPM. The pH of the sample was taken using the Jenway Mettler Toledo 3510 pH meter. The indicator electrode was pre-calibrated using buffer solution (4 and 7), the pH of both soil and biochar was measured, and all samples were run in triplicate to acquire a promising result.

2.3.2. Soil and Biochar Metal Analysis

Three to five (3 to 5) grams of the sample was weighed and put into an XRF clean soil pot covered with a mylar thin film (6.0 μm) over the bottom and secured with a ring. A field portable Niton XL2 Gold handheld XRF device was fixed within a holding platform and was used to dictate the presence of heavy metals in the samples, each sample was analyzed at 240 sec. The device was calibrated to a standard using certified reference 73308 and each sample was analyzed in triplicates.

2.4. FTIR Analysis

FTIR is a powerful analytical technique used to study the inorganic and organic properties of soil sediments. FTIR uses infrared to measure the amount of surface functional groups at a wavelength range of 600 - 4000 cm^{-1} will be identified from the corresponding peak. The FTIR analysis would indicate whether functional groups of biochars are obtained at different pyrolysis heating, samples if similar, and whether aromatic and aliphatic groups are predominant as seen in [42]. Before each use of the FTIR, an internal calibration of the instrument was performed. Surface functionality was investigated with a Thermo Fischer Nicolet IS-10 OMNIC machine using single bounce attenuated total Reflection-Fourier transform infrared (ATR-FTIR) spectroscopy with a diamond Internal Reflection Element (IRE), an acquisition time of 1mins 40secs and a total of 100 scans per sample instead of 16 scans, *i.e.*, for better signal-to-noise ratio and higher accuracy spectrum range between (600 - 400 cm^{-1}) resolution. SWP550 and SWP770 (<63 μm) were used in the experiments. The smaller the particles size the better contact between the knob and sample. To measure the transmittance and absorbance of the FTIR machine biochar sample was used (**Plate 1**).

2.4.1. Scanning Electron Microscope Analysis

Philips XL30 SFEG scanning electron microscope system was used to identify

the surface morphology, composition, and pore size of the biochar sample. However, it can also be used to determine qualitative chemical analysis of a sample. The biochar sample was placed on the adhesive carbon tape on an aluminum stub where the electrons in the beam interact with the sample and give out different signals to achieve information. Micrographs of various magnifications were produced and chosen for qualitative analysis.

Plate 1. FTIR machine.

2.4.2. Microcosm Experiments

A microcosm experiment was conducted to detect the release of heavy metals from contaminated soil to the overlying water from two different soils upon water inundation. 500 mL plastic bottles were used as reactors prior, to the experiment, the bottles were washed and rinsed with nitric acid, deionized water, and then dried. All bottles were labeled before analysis and three treatments were used for each sample. Treatment 1 was a control with no added organic matter, Treatment 2 and 3 had 5 g of grass clippings added to the samples (**Table 1**). A Grass clipping was added to know if the quantity of organic matter present has an impact on the mobilization of heavy metals [41] [43]. In each bottle, 50 g of soil was added, 200 mL of Ultra-pure water (18.2MX cm) was added to the sample, and the grass was added to relevant treatments. Afterwards, the bottle was capped and agitated by hand for a minute then allowed to settle for 5 minutes. The temperature maintained throughout the experiment was 25 ± 10˚C. The experiments were run for 15 days, during the incubation period, measurements were taken at set intervals, *i.e.*, after 0, day 1, day 2, day 5, day 10, and day 15 respectively. The pH, EC, and DO were measured on the set days using a pH meter (Jenway-3510), EC meter (Mettler Toledo), and DO meter (Oxyguard Handy MK1 DO). 10ml of the samples was taken at these intervals and filtered using a 0.22 μm syringe filter. A centrifuge tube was used to store the solution and 2 drops of nitric acid was added to the sample to bring down the pH and prevent metal precipitation and the solution was stored in the fridge at 4˚C.

Table 1. List of samples.

ID	Soil (gram)	Grass (gram)	Biochar (gram)	Water (mL)
T1	50	5	0	150
T2	50	5	0.5	150
T3	50	5	2	150
T4	50	0	0.5	150

2.5. Statistical Analysis

The equipment used in the laboratory for this study was of high standard and precision, all the apparatus and bottles were washed thoroughly with ICP-grade water to avoid contamination. All the experiments were conducted in triplicates to ensure accuracy and reliability. The treatments for pH and DOC were analyzed to determine the mean values and standard deviation of the soils respectively. All statistical analysis was carried out using IBM SPSS software version 23.

3. Results and Discussion

3.1. XRF Results

The result from the XRF shows that the concentration was high for both iron and manganese, while calcium had the lowest. Collectively the concentration of inorganic pollutants was higher than organic pollutants for the biochar samples. For the soil samples arsenic and manganese had the highest concentration level. While ICP-Microwave Digestion results reveal that iron and manganese had the highest concentration level similar to the XRF results. However, cadmium was under the detection limit (**Table 2**).

Table 2. Concentration level of heavy metal dictated by XRF.

	As	Cd	Cr	Fe	Mn	Pb	Zn	Cu
Mean	33.85	Udl	3.74	6874.09	265.00	78.18	94.49	182.25
Std. Dev	57.40	Udl	6.68	11534.69	349.11	140.96	159.43	309.66

3.2. FTIR Analysis

The results of the biochar samples identified the major and minor peaks. The FTIR showed that biochar composition has an impact on pyrolysis temperature. Increasing temperature up to 700˚C resulted in decreased peak intensities. The most identifiable peak occurred in 1558 - 1568. Three peaks were seen between 800 - 1600 which can be associated with the C-H bonding. Notable peaks include the C=C group, C-H, and CO bonding. However, at 700˚C fewer peaks occurred which is a result of the decrease in the number of FTIR bands. Large peaks are usually not seen with FTIR spectra of highly aromatic chars (**Figure 1**).

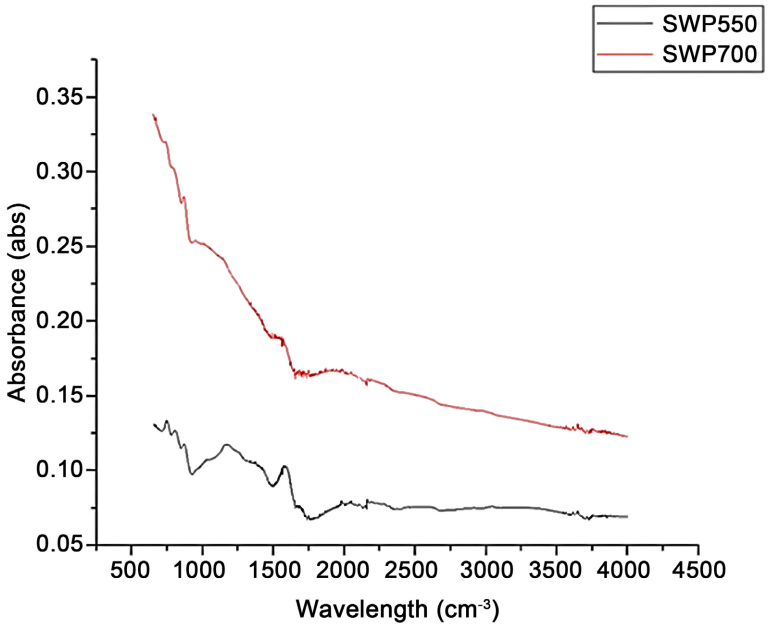


Figure 1. FTIR spectra for SWP550 and SWP700.

3.3. pH and EC for Biochar and Soil

The result shows that the pH for biochar is alkaline in nature. This can be due to the liming effect of biochar on acidic soils. However, the pH of the soil was acidic which shows that the soil is contaminated with heavy metals due to anthropogenic activities in the area (**Table 3**).

Table 3. pH and EC for the mixed biochar and soil.

Biochar	pH	EC (dS/m)
SWP550	7.70 ± 0.72a	29.73 ± 0.80c
SWP700	9.03 ± 0.50b	84.37 ± 1.06b

Means of each parameter with different letters at the same interval indicate a significant difference ($p < 0.05$).

3.4. SEM Analysis

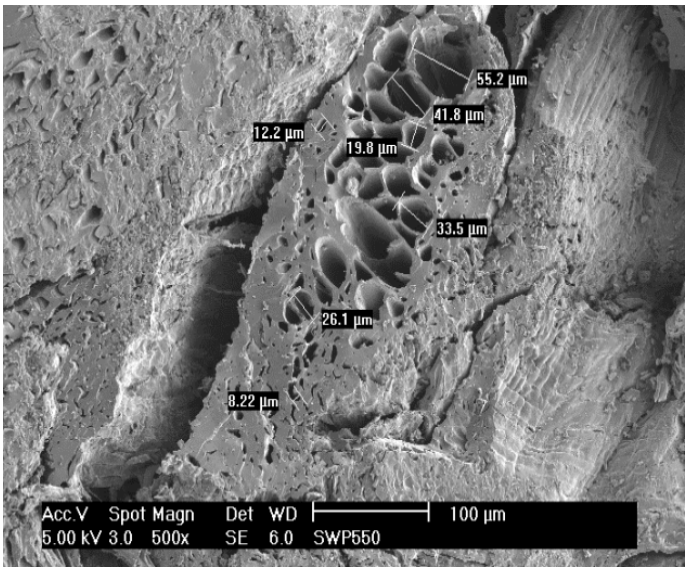
A great difference was observed in the surface structure of the biochars (550 and 700). The soft wood pellets showed many shapes with a size range from (5 - 500 μm) micro to macro pores. Biochar at 550 was glossy and 700 were flaky. Different magnifications were visible, larger pores were observed more in SWP700 as compared to SWP550, this can be due to the pyrolysis reaction rate at high temperatures. **Plate 2(a)** & **Plate 2(b)** show SEM images of biochar at SWP550 and SWP700 magnification.

3.5. Microcosm Experiment

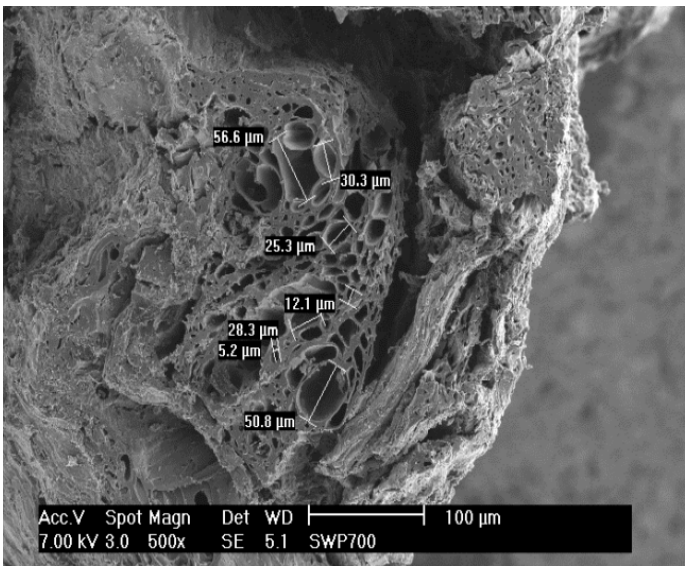
3.5.1. Changes in pH, EC, and DO during the Period of the Incubation Experiment

Roughly 1 hour after the start of the experiments, the pH, EC, and DO level was

measured. The DO level of the sample without organic matter was higher than the ones with organic matter (grass chips). However, the controls of the samples dropped drastically within the hour. After the 1st day, DO continued to decrease until the 15th day while that of the controls dropped but started increasing on the 10th day till the end of the experiments. DO of treatment 1 and treatment 2 (SWP550 & 700) having organic matter retained a low level all through the experiments. As the days went by the EC for the T_1, T_2, T_3 & T_4 (SWP550 and SWP700) with organic matter and without organic matter continued to increase till the end of the experiments. The pH ranged from 4.20 - 5.97 for the controls, T_1 - T_4. The trend shows pH increased over time for all the treatments (with and without organic matter) in **Figure 2(a)-(c)**.

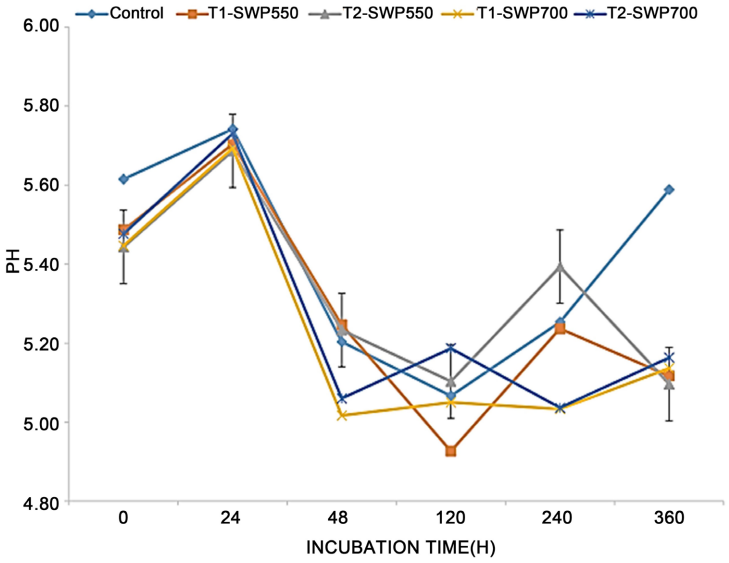


(a)

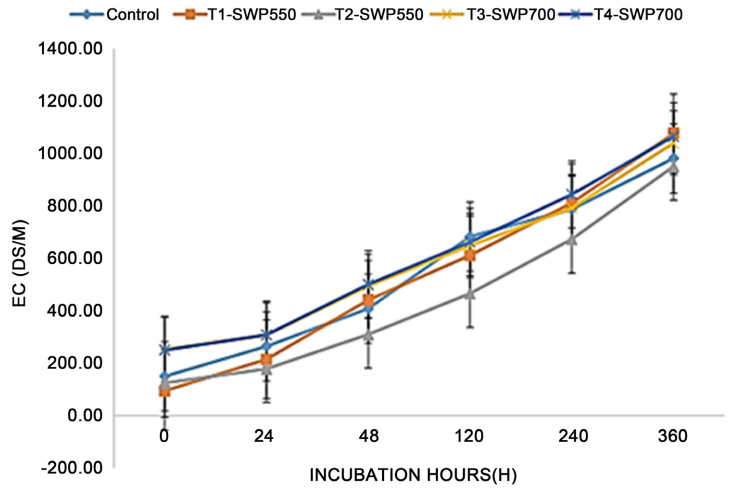


(b)

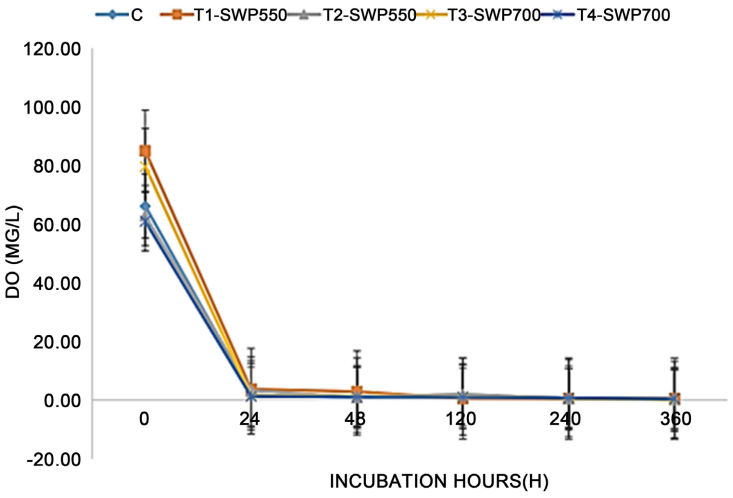
Plate 2. Micrograph results of biochar SWP550 (a) and SWP700 (b).



(a)



(b)



(c)

Figure 2. It shows changes in pH, EC & DO during incubation.

3.5.2. Iron (Fe) and Manganese (Mn)

The concentration of Fe in the incubation experiment was low for the controls but started increasing at the 120th hour till the end of the incubation time. For all the treatments T_1, T_2, T_3, and T_4 (SWP550 & 700) with organic matter, the concentration of Fe increased as the days passed till the end of the experiment. For T_3 (SWP700) the concentration was much higher due to less biochar than T_4 (700) having more biochar, the trend of Fe increased throughout the experiment. The concentration of Mn was low at the start of the experiments, there was a clear trend where the concentration of Mn increased for the controls and treatments with organic matter. However, it was observed that the concentration of T_2 (SWP550) was higher than T_1 (SWP550) while the reverse is the case for SWP700 (**Figure 3**).

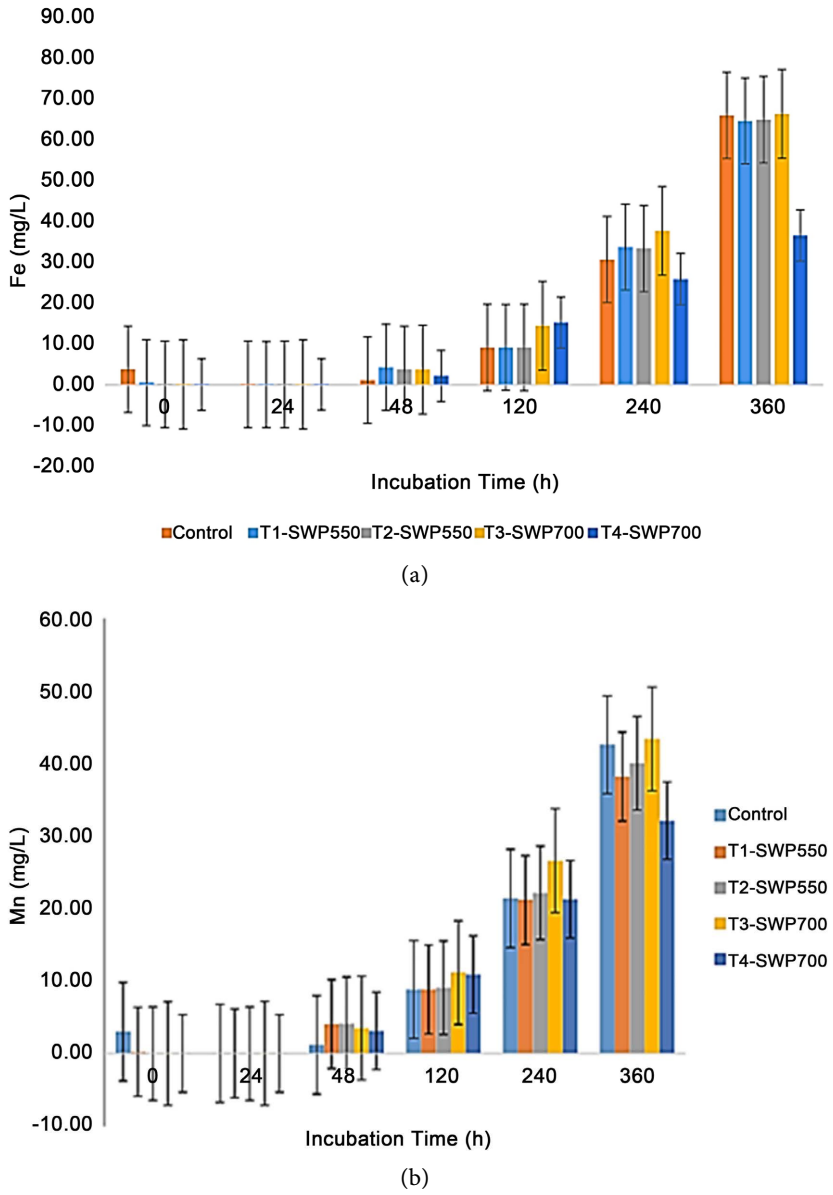


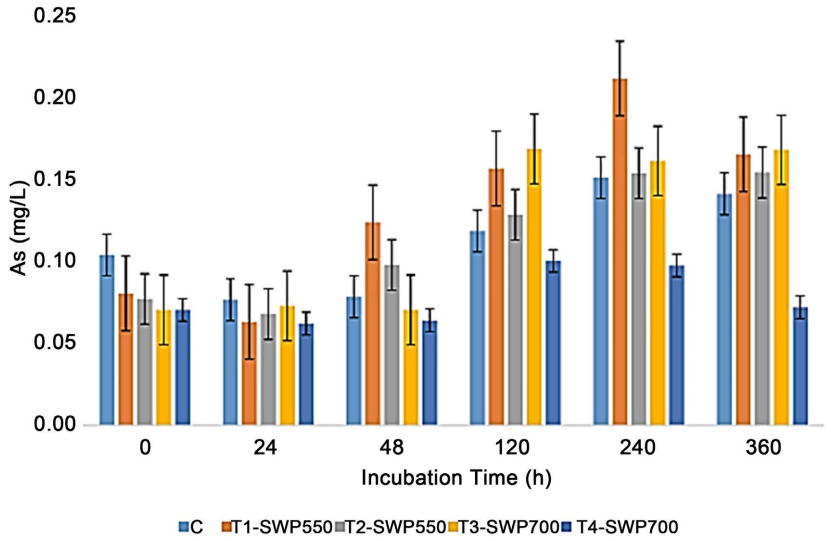
Figure 3. Fe and Mn concentration during the inundation period.

3.5.3. Arsenic (As)

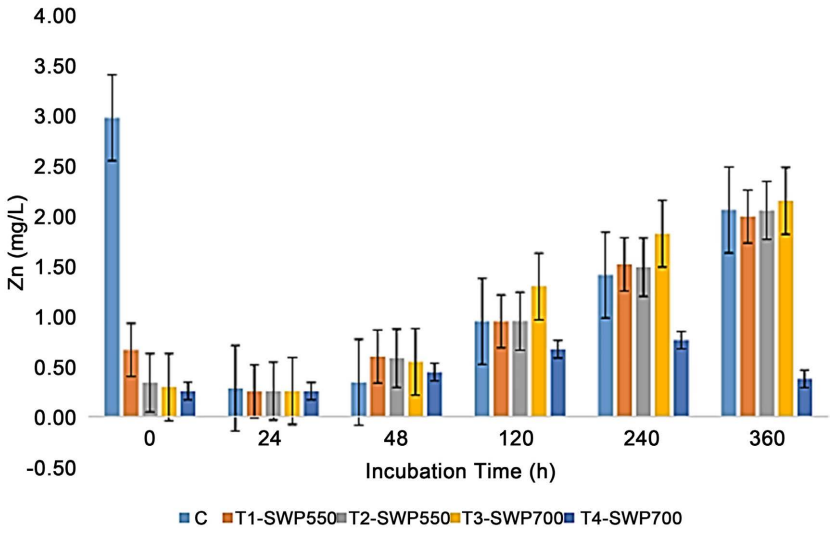
The concentration of Arsenic (As) increased from the 120th hour for all the treatments SWP550 (T_1 & T_2), SWP700 (T_3 & T_4), and controls except for T_1 (SWP550) which was low towards the end of the experiments. Different trends were noticed till the end of the incubation period. However, the concentration taken at the 360th hour was low and the differences observed were insignificant.

3.5.4. Zinc (Zn)

An increase in the concentration of Zn for all the controls and treatments was observed. However, the control sample collected at 0 hours was much higher than the 360th hour. The concentration of Zn for T_3 (SWP700) was always high but decreased at the end of the experiment and the difference is minor on a statistical level Figure 4.



(a)



(b)

Figure 4. As and Zn concentration during the inundation period.

3.5.5. Lead (Pb), chromium (Cr), Cadmium (Cd) and Copper (Cu)

Pb concentration was low at the start of the experiments for controls, treatments 1 & 2 for the samples. As the trend goes the concentration was higher for all the samples except for SWP550 (T_1 & T_2) and SWP700 (T_3 & T_4) which showed a sudden decrease at the 360th hour of the experiment. Cr in all the samples was not significant as just a little was detected for all the treatments and controls at the 360th hour. As shown in Table 1. Cd was detected at the start of the incubation period for all the samples. However, as the days passed by Cr was no longer detected till the end of the incubation period. Cu was under the detection limit as a small amount was seen at 0 hours of the experiment (Table 4).

Table 4. Concentration level of metals recorded at different days of the experiment.

Metal (ppm)	Treatment	Day 0	Day 1	Day 2	Day 5	Day 10	Day 15
Cadmium	C	0.09	0.09	0.04	0.01	0.02	0.03
	T1-SWP550	0.08	0.09	0.03	0.01	0.02	0.03
	T2-SWP550	0.09	0.08	0.01	0.02	0.03	0.02
	T3-SWP700	0.09	0.09	0.01	0.02	0.02	0.03
	T4-SWP700	0.1	0.08	0.03	0.01	0.04	0.01
Chromium	C	0.03	0.03	0.02	0.03	0.05	0.08
	T1-SWP550	0.03	0.03	0.04	0.06	0.04	0.07
	T2-SWP550	0.04	0.03	0.06	0.06	0.03	0.06
	T3-SWP700	0.04	0.03	0.05	0.08	0.05	0.07
	T4-SWP700	0.04	0.04	0.03	0.02	0.03	0.09
Copper	C	3.69	Udl	udl	udl	0.01	udl
	T1-SWP550	Udl	udl	udl	udl	udl	udl
	T2-SWP550	Udl	udl	0.01	udl	udl	0.02
	T3-SWP700	Udl	0.03	udl	udl	0.01	udl
	T4-SWP700	0.02	udl	udl	0.02	udl	udl
Lead	C	0.1	0.12	0.1	0.16	0.13	0.08
	T1-SWP550	0.13	0.15	0.09	0.11	0.17	0.17
	T2-SWP550	0.11	0.12	0.09	0.14	0.15	0.13
	T3-SWP700	0.12	0.1	0.14	0.28	0.11	0.14
	T4-SWP700	0.11	0.11	0.06	0.04	0.14	0.12

4. Discussion

This study aimed to identify the concentration of heavy metals in contaminated soil and how biochar can effectively retain these metals under flooding conditions. The XRF analysis was used to identify the presence of heavy metal concentration in the soil. The heavy metal concentration from highest to lowest for the soil samples is in order of As > Fe > Mn > Cr > Zn > Pb > Cu. This shows that arsenic had the highest concentration for the soil samples which might be as

a result of heavy metal accumulation due to the presence of particle-size matter. The ICP-microwave digestion was used to analyze the amount of heavy metal present, however, this method is not a total extraction technique. The concentration of heavy metals from highest to lowest for the soil is Fe > Mn > Cu > Zn > Pb > As compared to the XRF which had the highest concentration. This means that the ICP technique is not the best option for analyzing arsenic due to interference that exists in the emission spectra.

FTIR analysis was conducted to find the relative contribution of the chemical functional group and show the sample's aromatic nature. Also as a characterization tool, FTIR provides a clear picture of the effect of pyrolysis temperature on biochar chemical composition. A general observation showed that an increase in temperature resulted in a decrease in peak intensities. The most identifiable peak occurred in 1558 - 1568 cm^{-1}. Three peaks were seen between 800 - 1600 cm^{-1} which can be associated with the C-H bonding. Most of the peaks observed in biochars having high pyrolysis temperatures can be found in the fingerprint region between 500 - 1800 cm^{-1}. The peak intensity around 1600 cm^{-1} relates to C-C stretching vibration in aromatic compounds [44], yet was less visible at 700˚C. The peak intensity related to aromatic nature increases at 550˚C while the peak becomes delicate at 700˚C. A study by [45] explained that peaks from 710 - 2500 cm^{-1} are associated with carbonates. These peaks can be seen in biochar spectra produced at 550˚C temperature and are slightly visible at 700˚C. This means that a decrease in peak is observed at 700˚C as large peaks are usually not seen with FTIR spectra of highly aromatic chars.

This study showed that biochar pH ranged from (7 - 9) which is alkaline in nature. This can be a result of the biochar liming effect on acidic soils which shows that the soil surface is highly contaminated with heavy metals due to past industrial activities. Also, environmental hazards such as acid precipitation mobilize heavy metals and could increase the soil pH. **Table 3** shows that EC indicates the amount of soluble ions in the soil. SWP700 had the highest EC compared to SWP550. Soil's ability to exhibit both cations and anions is dependent on EC. This explains that at high temperature EC also increases and the statistical difference observed was ($p < 0.05$).

The SEM images represent biochar at different temperatures (550 and 700) **Plate 2**, SEM is an efficient tool used to characterize the spatial distribution of biochar organic composition. The soft wood pellets showed several shapes with a size range from (5 - 500 μm) micro to macro pores. Biochar at 550 was glossy and 700 were flaky. Different magnifications were visible, larger pores were observed more in SWP700 as compared to SWP550, this can be due to the pyrolysis reaction rate at high temperatures. Different shapes in macropores and mesopores were observed as biochar porosity structure was determined, which explains the biochar's large surface area.

The result reveals that DO with treatments having organic matter was low barely 1 hour after the start of the experiments compared to the control. This implies that DO consumption was fast as a result of the organic matter in the

overlying water on which the bacteria feed. After the 1st day, DO continued to decrease until the 15th day while that of the controls dropped but started increasing on the 10th day till the end of the experiments. DO of treatment 1 and treatment 2 (SWP550 & 700) having organic matter retained a low level all through the experiments. This is because more oxygen is consumed as the days go by, and the EC for the T_1, T_2, T_3 & T_4 (SWP550 and SWP700) with organic matter and without organic matter continued to increase till the end of the experiments. The highest concentration was seen on the 360th hour. This showed how the ions dissolved in the overlying water. The increase was due to the release of soluble salts contained in the biochar used. Also, the increase can be a result of the rich ash contents contained in the biochars (**Figure 2**).

Fe plays a major role in overlying water as it affects the exchange of trace metals. The grass chippings added to the treatments result in microbial decomposition. Studies revealed that the microbial reduction was a result of ferric iron (Fe^{3+}) which serves as an electron receptor [3] [44] [46]. The Fe mobilization was obvious at the 120th hour for treatment with organic matter. The set experimental conditions reveal that the amount of organic matter in the treatments affected anaerobic Fe reduction. Also, the concentration for T_3 (SWP700) was much higher due to less biochar than T_4 (SWP700) having more biochar. However, Fe concentration in SWP550 was lower as compared to SWP700 which shows that Fe released during the incubation period is affected by the presence of Fe in the soils. For the controls without grass chippings, a small amount of Fe was released. The reason might be due to the organic debris present in the samples. A significant difference was observed at the 120th hour for both control, T_1 and T_2. Fe on the 120th hour for T_3 showed significant differences compared to the 48th hour and 360th hour.

The equation shows Fe reduction during the water inundation experiment.

$$Fe(OH)_3 + 3H^+ \rightarrow Fe^{2+} + 3H_2O \quad (1)$$

Manganese was released from the soil to the overlying water in all the treatments which can be attributed to anaerobic reduction of manganese oxide (MnO). The addition of organic matter resulted in the release of Mn just like Fe, the trend increased till the end of the incubation period. However, the release of Mn for T_2 (SWP550) was higher than for T_1 (SWP550) while the reverse is the case for SWP700. This can be attributed to the small amount of biochar present in the samples. A significant difference was observed for the controls at the 360th hour compared to the beginning of the experiment. For T_1 and T_2 there was a big difference at the 120th hour, 240th hour, and 36th hour which means that Mn increased and was released to the environment.

Arsenic release during the experiment could be observed and might be due to the reductive dissolution of iron. Ironbound with arsenic to give iron arsenate, while different trends were noticed during the experiments, the concentration of As was high at the 120th hour for all the controls and treatments except for T_1 (SWP550) which was low as compared to T_3 & T_4 (SWP700). This suggests that

high temperature also affected the amount of heavy metal released during the experiment. The amount of As in a particular time can be known and determined by the rate of immobilization. A significant difference was observed at the 360th hour for both control and T_2. The As on the 24th hour and 120th hour for T_3 showed significant differences compared to the 48th hour and 360th hour.

Like iron and manganese, the release of zinc was due to the reductive dissolution of Fe and MnO. The concentration of Zn for the controls and treatments increased but the SWP700 was high till the 240th hour. However, the concentration of SWP700 at 360th hour was lower. This might be due to re-immobilization which occurred through hydrolysis. As described in the equation;

$$Zn^{2+} + H_2O \rightarrow Zn(OH)_2 + 2H^+ \quad (2)$$

For the control, T_3 and T_4 no significant difference was observed as compared to the 120th hour of T_1 and T_2 where the trend increased. The concentration of lead was low at the start but increased as the days went by. However, Pb release can be attributed to the partition of metals from different phases.

As a result of electrostatic attraction, chromium is reduced from Cr (VI) to Cr (III) to form chromium hydroxide. Biochar serves as an efficient reluctant due to the surface functional group and larger surface area. This mechanism explains why chromium was not detected for most of the samples, *i.e.*, controls and treatments. Cd and Cu were barely detected throughout experiments. This might be a result of the small amount of both metals present in the soils. The findings from this research show that SWP550˚C is less effective compared to SWP700˚C. Also, a large amount of biochar at 700˚C is essential to effectively retain heavy metal in contaminated soil. The effect of biochar depends on feedstock type and pyrolysis temperature. However, Tang [47] used hardwood biochar to multi-contaminated elements (As, Cu, Cd, and Zn) where they observed AS and Cu mobilized compared to Cd and Zn which were immobilized in the soils, for biochar to be used as a soil amendment, a cost-benefit analysis should be carried out. However, the cost of biochar is dependent on many factors such as feedstock type, temperature, production scale, distribution, and handling.

5. Conclusion

This study shows that softwood pellet biochar serves as a tool for soil amendment and can remediate contaminated soil. Biochar serves as a cheaper and greener environmental sorbent. However, the type of biochar used in this study shows that SWP700 in large amounts is more efficient than SWP550. As regards contaminant removal, one type of biochar might not be appropriate. Studies show that biochar can increase the strength of metal toxicity in soils. It is important to investigate biochar efficacy in the stabilization of contaminants before using the biochar. The results of the research showed that SWP700 was more effective compared to SWP550. The reason behind the low efficiency can be attributed to certain factors such as pyrolysis temperature, feedstock type, contact time, and pH. Based on this further assessment needs to be done on the risks

that may arise due to high levels of heavy metal in contaminated land and an investigation on the type of biochar properties and pyrolysis conditions should be carried out.

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Authors' Contributions

Kyari Umar Donuma: Investigation, Data collection, Writing-original draft preparation. Limin Ma: Supervision, Validation, Funding, Project administration, Supervision, Resources, Validation, Funding, Writing-review & editing. Shu Xingquan, Yu Haiyan, Zhang Weiwei, Bu Chengcheng, Wang Yong-Sik, Luo Jiahong, Chen Guangyao, Yu Jinpeng, Zhang Ru, Han Yuchen, Zeng Haoyu, Matthew S. Wisseh, Amina Grema Mustafa, Mohammad Auwal Saidu, Mufidat Maman Khan: Writing-review and editing.

Ethical Approval

All authors have read, understood, and have complied as applicable with the statement on "Ethical responsibilities of Authors" as found in the Instructions for Authors and are aware that with minor exceptions, no changes can be made to authorship once the paper is submitted.

Data Availability

The authors do not have permission to share data.

Conflicts of Interest

The authors declare they have no competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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