AgroLife Scientific Journal - Volume 14, Number 1, 2025
ISSN 2285-5718; ISSN CD-ROM 2285-5726; ISSN ONLINE 2286-0126; ISSN-L 2285-5718

BIOCHAR FROM PULP AND PAPER MILL SLUDGE: CO-PYROLYSIS WITH BENTONITE, NUTRIENT RETENTION AND LEACHABILITY

Viktoriia HETMANENKO[1], Svitlana KRYLACH[2], Yevhen SKRYLNYK[2], Maxim POPIRNY[2], Angela KUTOVA[2]

[1]Natural Resources Institute Finland, Latokartanonkaari 9, 00790, Helsinki, Finland
[2]National Scientific Center "Institute for Soil Science and Agrochemistry Research named after O.N. Sokolovsky", 4 Mykhailia Semenka Str., 61024, Kharkiv, Ukraine

Corresponding author email: viktoriia.hetmanenko@luke.fi

Abstract

Pulp and paper mills generate substantial sludge as a byproduct of wastewater treatment, offering a viable feedstock for biochar production. This study examines the potential of biochar derived from pulp and paper mill sludge to enhance nutrient management in manure handling and soil systems. Fiber sludges, classified as low-nutrient fiber and nutrient-rich fiber, were pyrolyzed at 450°C, both individually and with a mineral additive. Co-pyrolysis with bentonite significantly increased the specific surface area and porosity of the biochar. Nutrient adsorption experiments using liquid pig slurry showed that the biochars retained 1.14-1.57% of total nitrogen and 0.54-0.78% of total phosphorus, with bentonite-enhanced biochars demonstrating superior retention. Soil incubation and rainfall simulation experiments confirmed that nutrient-rich fiber biochars effectively reduced phosphorus leaching compared to conventional mineral fertilizers, whether produced alone or with bentonite. However, biochars from low-nutrient fiber led to nitrogen losses similar to mineral fertilizers. The Fourier infrared spectroscopy analysis revealed greater carbon stability in nutrient fiber biochars, highlighting the role of bentonite in enhancing biochar's chemical stability.

Key words*: pyrolysis, sorption, nitrogen, phosphorus, percolation losses*

INTRODUCTION

Pulp and paper mills generate significant quantities of sludges as byproducts of wastewater treatment processes. These sludges are derived from primary and secondary treatment of wastes originating from virgin wood fiber sources, recycled paper products, and non-wood fibers (Camberato et al., 2006). The land application of sludges is increasingly being adopted as a common method for its utilization. Pulp and paper mill sludge (PPMS) is rich in organic matter and composed of cellulose, hemicellulose, and lignin, making it a suitable feedstock for biochar production (Leng et al., 2021). Recently, pyrolysis has been recognized as a suitable method for treating PPMS, as the resulting biochar demonstrates strong adsorption capabilities for various pollutants along with nitrogen (N) and phosphorus (P) compounds (Reis et al., 2022).
Pyrolysis temperature plays a crucial role in shaping the physicochemical properties of biochar (Tomczyk et al., 2020). It significantly affects composition, surface characteristics, and cation exchange capacity (CEC), which are key factors determining its adsorption ability (Ortiz et al., 2020). Biochars produced at lower pyrolysis temperatures (300-500°C) retain more functional groups, improving ammonium retention, while those produced at elevated temperatures (> 700°C) exhibit increased porosity but have a lower density of functional groups (Munar-Florez et al., 2021).
Previous studies have demonstrated that biochar can efficiently adsorb nitrogen, particularly ammonium (NH_4^+), while also limiting its mobility and reducing the risk of leaching into water bodies (Yao et al., 2012; Kammann et al., 2017). Zhang et al. (2022) demonstrated that PPMS-derived biochar exhibits high efficacy in removing P from water, with a maximum adsorption capacity of 25.19 mg P per g of biochar. The presence of CaO, derived from $CaCO_3$ additives in PPMS, has been observed to enhance phosphate precipitation, thereby further improving biochar efficiency in P removal (Yin et al., 2018).
Bentonite, known for its high cation exchange capacity and surface area, enhances the

structural and functional properties of biochar when co-pyrolyzed with organic waste materials like PPMS. The study by Cao et al. (2022) demonstrated that a composite of bentonite and sludge biochar enhances adsorption reactions toward pollutants. Hagemann et al. (2018) showed that biochar-clay composites improve NH_4^+ adsorption by 30-50% compared to unmodified biochar.

The use of biochar can effectively prevent nutrient leaching by enhancing soil aggregation, improving water retention, and increasing CEC, thereby reducing the movement of water-soluble nutrients through the soil (Atkinson et al., 2010; Yuan & Xu, 2011; Borchard et al., 2019). The ability of biochar to reduce nutrient leaching varies with soil type, showing greater effectiveness in sandy or low-organic-matter soils where natural nutrient retention is limited (Laird et al., 2010).

Manure often contains N and P in ratios that do not align with crop requirements. Applying manure based solely on N needs of crops can lead to P accumulation in soils, increasing the risk of runoff and water contamination. Manure separation technologies and strategic nutrient management practices play pivotal roles in optimizing the use of these nutrients while mitigating their potential negative impacts on ecosystems. However, liquid manure, while rich in soluble N, poses logistical challenges due to its bulkiness, further complicating efficient nutrient management (Dadrasnia et al., 2021).

Biochar can be a promising tool for adsorbing and retaining N and P from liquid manure. In manure-amended soils, biochar amendments have been shown to reduce dissolved P leaching by up to 60%, as demonstrated by Beesley et al. (2010). Developing bio-based fertilizers using nutrient-loaded biochar could enable targeted application of N and P, minimizing imbalances and reducing runoff risks. Tailored biochar formulations for specific feedstock properties, pyrolysis temperatures, and mineral additives can maximize nutrient retention while mitigating environmental losses.

The aim of this study is to assess the effectiveness of pulp and paper mill sludge-derived biochars, co-pyrolyzed with bentonite, in retaining nitrogen (N) and phosphorus (P) from liquid manure and reducing their leaching after soil application.

MATERIALS AND METHODS

Biochar production. Pyrolysis experiment utilized fiber sludges sourced from the pulp and paper industry, which were processed and refined in different ways:

1. Low-nutrient fiber (LNF): nutrient-poor cellulose material derived from the pre-clarifier of the cardboard machine process water. This material was removed as a semi-dry mass using a wire sieve and consists of cellulose fibers that are too short for the final paper product.
2. Composted mixed pulp mill sludges or nutrient fiber (NF): these sludges originate from the mill's biological water treatment process and contain N and P, and other essential nutrients.

Bentonite was chosen to co-pyrolysis with LNF and NF to study the effect of mineral structures on the characteristics of biochar.

LNF and NF were mixed with bentonite (b) at a 100:10 ratio by volume. The feedstocks were then pre-dried at 37°C, ensuring a dry matter content exceeding 90% before undergoing pyrolysis. Pyrolysis was conducted using a batch-type laboratory-scale pyrolysis system at the Natural Resources Institute Finland, Jokioinen, with a maximum pyrolysis temperature of 450°C. The yields of biochar and liquid were determined through direct weighing, while gas production was estimated based on the difference between the initial biomass mass and the sum of biochar and liquid yields.

Sorption experiment. The produced biochar samples were gently crushed and sieved to obtain a particle size fraction of <1 mm, which was then used for nutrient sorption experiment. 10 mL of biochar was placed in a 250 mL flask with 100 mL of liquid pig slurry (PS). The suspension was shaken for 24 hours using a rotating shaker at room temperature. The suspensions were filtered using a 1 mm sieve. Each treatment was conducted in triplicate to ensure reproducibility.

The liquid fraction of pig slurry used for sorption experiment contained 15% dry matter and 2.4 kg/m³ of total nitrogen, 0.7 kg/m³ of total phosphorus (P_2O_5), 0.4% of ammonium nitrogen ($N\text{-}NH_4$).

Soil incubation experiment. Following the sorption experiments, loaded biochars and a mineral fertilizer were mixed with 1 kg of air-dried soil at an $N_{100}P_{50}$ application rate. A control treatment with no fertilizer was included. Each treatment was replicated three times to ensure statistical reliability. Soils were moistened to 70% of water holding capacity using deionized water and incubated at 20°C for three weeks. Containers were covered with perforated plastic to minimize evaporation. Soil moisture was monitored twice a week by weighing, and evaporated water was replenished with deionized water. The soil used was clay soil with a pH of 5.7, 60% of clay and 4.4% total carbon.

Rainfall simulation test. After three weeks of incubation, the soil samples were prepared for rainfall simulations by packing the soil into 15-cm diameter PVC cylinders, following the methodology of Uusitalo et al. (2012). A nylon mesh was placed at the bottom of the cylinders. A 1 cm layer of coarse quartz sand was added to ensure drainage. The incubated soil was packed to a 7 cm depth within the column. Simulated rainfall was applied at a rate of 5 mm h^{-1} using a stationary drop-former rainmaker. Percolated water was collected through a drainage hole at the base of the column. Leachate was collected in acid-washed 100-mL plastic bottles. Three separate 100-mL water samples (totaling 15-20 mm of rain) were taken for each treatment.

Chemical and physicochemical methods of analysis. The Brunauer-Emmett-Teller (BET) method was applied to calculate the specific surface area (SSA). The total nitrogen content of biochar samples was determined using the Kjeldahl method, following standards SFS EN ISO 20483:2013, EN ISO 5983-2, and AOAC 2001.11, with a FOSS Kjeltect 8400 analyzer. Ammonium nitrogen (NH_4-N) concentrations were determined using a continuous flow analyzer (Skalar San++ System).

Total phosphorus (Ptot) in both pure biochars and pig slurry-loaded biochars was determined after autoclave-assisted acid digestion in an autoclave (120 °C, 100 kPa, 30 min) following the method of Turtola, 1996 and quantified by molybdate colorimetry (Murphy & Riley, 1962). Carbon contents were analyzed by dry combustion using a LECO TruMac CN analyzer.

Water samples collected after rainfall simulation were immediately analyzed for turbidity 2100AN IS Turbidimeter (Hach). The pH and electrical conductivity (EC) of the percolated water were measured using Mettler Toledo InLab Expert Pro-ISM and InLab 731-ISM electrodes, respectively. Total phosphorus (Ptot) in percolate samples was determined after acid peroxodisulfate digestion (Turtola, 1996; Murphy & Riley, 1962). Analyses of PO_4-P and dissolved total nitrogen (DTN) were performed with a continuous flow analyzer (Lachat QuickChem 8500).

The Fourier Infrared Spectroscopy (FTIR) of biochar samples was performed using the Agilent Technologies Cary Spectrometer 630 supplied with Diffuse Reflectance and Fourier Transformation in the standard measurement area of 1000-4000 cm^{-1} (in a potassium bromide compressed tablet).

Statistical analyses. Differences between treatments were evaluated using ANOVA test. Pairwise comparisons between treatments and soils were performed using two-sample t-tests with a two-tailed hypothesis. Statistical significance was set at $\alpha < 0.05$ for all tests.

RESULTS AND DISCUSSIONS

Biochar characteristics. Among the biochar yields obtained from the pyrolysis of PPMS, NF co-pyrolyzed with bentonite (NFb) exhibited the highest yield (66.94 %) (Figure 1).

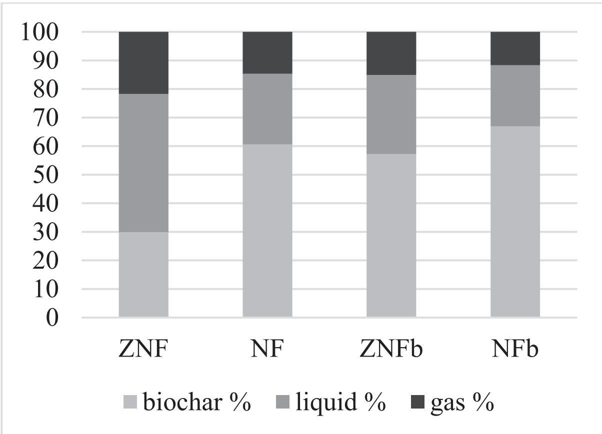

Figure 1. Biochar, liquid, and gas yield distribution (mass percentage) after pyrolysis of different feedstocks

NF biochar yielded more than twice the amount of LNF biochar, indicating that nutrient-rich feedstocks promote higher char formation. This finding aligns with the study by Wang et al. (2022), which emphasized the influence of feedstock composition on biochar yield. Additionally, the incorporation of bentonite led to a reduction in liquid and gas production in both LNF and NF feedstocks, further enhancing the solid biochar yield.

The BET analysis shows that LNF-derived biochar exhibits a significantly higher surface area (3.3 m²/g) and pore volume (0.0045 cm³/g) compared to NF biochar, which has a surface area of 1.7 m²/g and a pore volume of 0.0033 cm³/g (Table 1). This suggests that LNF biochar has greater adsorption potential. However, NF biochar has a slightly larger mean pore diameter (4.3 nm vs. 3.6 nm for LNF), which may influence its ability to retain nutrients.

Table 1. BET analysis of biochar samples

Sample name	LNF	LNFb	NF	NFb
SSA, m^2/g	3.3	12.1	1.7	4.2
Mean pore diameter, nm	3.6	4.4	4.3	5.5
Pore volume, cm^3/g	0.0045	0.017	0.0033	0.0073
µpores (<2.2 nm), cm^3/g	0.0011	0.0032	0.0005	0.0008
mesopores (2.2-50 nm), cm^3/g	0.0029	0.0127	0.0023	0.006
macropores (50 > nm), cm^3/g	0.001	0.001	0.001	0.001
µpores (<2.2 nm), %	24.4	18.8	15.2	11.0
mesopores (2.2-50 nm), %	64.4	74.7	69.7	82.2
macropores (50 > nm), %	11.2	6.5	15.1	6.8

The addition of bentonite significantly improved biochar properties. LNFb biochar exhibited 3.67 times higher SSA, and 3.78 times greater pore volume compared to to non-modified biochar. Similarly, NFb biochar showed 2.47 times higher SSA, and 2.21 times greater pore volume compared to NFb.

Previous studies also demonstrated that bentonite incorporation during pyrolysis increases surface area and porosity, thereby boosting adsorption capacity of biochar (Karod et al., 2022). Wang et al. (2022). proved positive effect of co-pyrolysis with bentonite on thermal stability of biochar, enhancing its resilience to mineralization. It is known that thermal conditions during pyrolysis play a crucial role in determining biochar properties. Higher pyrolysis temperatures (500-700°C) generally promote greater devolatilization, leading to an increase in surface area (Chatterjee et al., 2020). However, during co-pyrolysis with bentonite, temperatures exceeding 500°C can cause volatile organic compounds to recondense on the biochar surface, potentially blocking pores and reducing surface area (Chen et al., 2017).

The pH of the biochar samples ranges from 7.3 to 9.4, confirming their consistently alkaline nature, a characteristic commonly observed in biochars (Table 2). The hydrogen to carbon (H/C) ratio in the produced biochars falls within the acceptable limits set the EU Fertilizing Products Regulation 2019/1009 (European Union, 2019), ensuring its suitability for agricultural applications.

LNF biochar exhibits the highest carbon content (64.61% air dry matter), followed by NF biochar (52.20%).

The addition of bentonite significantly reduces the carbon content in both biochars. This reduction could be attributed to bentonite's catalytic effect during pyrolysis, promoting the decomposition of organic carbon into gases such as CO_2 or other by-products.

Nitrogen and phosphorus contents are highest in NFb (0.24% and 0.06%, respectively), reflecting an initially greater concentration of these nutrients in the feedstock. The NH_4-N levels remain constant (0.02%) across all biochars produced, suggesting minimal influence of pyrolysis conditions on ammonium nitrogen content.

Loading of nutrients from pig slurry (PS) had a neutralizing effect on biochar pH, while increasing the H/C ratio. Loaded biochars contain 1.14-1.57% of total N in dry matter, indicating strong sorption capacity across all biochars. Biochars from LNF with or without bentonite addition exhibit higher total N and NH_4-N content compared to NF biochar, which aligns with their higher SSA. The presence of bentonite in biochar samples further enhances NH_4-N retention due to modifying their adsorption properties. Specifically, bentonite slightly increases the retention of ammonium nitrogen in LNF biochar, while in NF biochar, it results in a more substantial increase of 25.88% compared to non-bentonite biochar. Total phosphorus (P_{tot}) is also effectively adsorbed by biochars during the loading process. The impact of bentonite on P sorption is more pronounced, with NFb showing 41% higher P content compared to NFb+PS. This aligns with previous findings where biochar derived from PPMS exhibited increased phosphate adsorption due to the formation of Fe–O–P ternary complexes and calcium-based precipitation mechanisms (Zhang et al., 2022). Similarly, Xiang et al. (2020) demonstrate that co-pyrolysis with bentonite enhances biochar's ability to adsorb NH_4^+ and PO_4^{3-} by as much as 40%, a result attributed to bentonite's role in forming stable mineral-nutrient complexes.

Table 2. Selected chemical characteristics of pure biochars and pig slurry-loaded biochars

Sample	pH	C_{tot}	H	P_{tot}	N_{tot}	NH_4-N
		(%, air dry matter)				
LNF	8.6	64.61	2.15	0.01	0.09	0.02
NF	9.3	52.20	2.11	0.03	0.12	0.02
LNFb	8.4	25.17	0.96	0.01	0.10	0.02
NFb	9.4	16.19	0.94	0.06	0.24	0.02
LNF+PS	7.3	42.15	3.52	0.09	1.95	0.83
NF+PS	7.9	37.58	2.56	0.15	1.14	0.63
LNFb+PS	7.3	29.28	2.54	0.54	1.57	0.90
NFb+PS	8.1	21.35	2.13	0.78	1.34	0.80

Nitrogen and phosphorus losses from biochar-amended soil after rainfall simulation. The ANOVA results revealed statistically significant differences ($p < 0.05$) in turbidity, electrical conductivity (EC), total phosphorus (P_{tot}), phosphate (PO_4-P), and dissolved total nitrogen (DTN), except pH across the treatments (Table 3).

Table 3. Characteristics of percolated water from biochar-amended soil (data are present as mean value ± standard error). Means denoted by a different letter indicate significant differences between treatment and control (a) and between treatment and NPmin ($p < 0.05$; n=3).

Treatment	Turbidity, NTU	EC, µS/cm	pH	P_{tot}, mg/L	PO_4-P, mg/L	DTN, mg/L
Control	32.8 ± 12.3	1320 ± 112	5.85 ± 0.12	0.159 ± 0.014	0.084 ± 0.002	155.19 ± 12.5
LNF	40.0 ± 1.5[a]	2092 ± 76[a]	5.26 ± 0.05	0.177 ± 0.012	0.100 ± 0.001	242.74 ± 15.6[a]
LNFb	33.9 ± 18.2	2037 ± 62	5.85 ± 0.05	0.172 ± 0.016	0.081 ± 0.010[b]	231.15 ± 1.4[a]
NF	16.6 ± 5.8	1856 ± 52[a]	5.75 ± 0.12	0.188 ± 0.006	0.105 ± 0.003	206.18 ± 17.2
NFb	20.4 ± 6.7	1645 ± 198	5.78 ± 0.08	0.155 ± 0.003	0.084 ± 0.005[b]	180.44 ± 25.6
NP_{min}	16.6 ± 10.2	2438 ± 61[a]	5.69 ± 0.10	0.310 ± 0.132[a]	0.256 ± 0.125[a]	294.19 ± 8.5[a]

Mineral fertilizer (NP_{min}) exhibited significantly higher EC values, indicating a higher concentration of dissolved salts, likely due to the rapid solubilization of its mineral nutrients. Substantial PO_4-P and DTN leaching was observed from the soil amended with NP_{min}, posing an increasing risk of water pollution. Meanwhile, biochars modified with bentonite demonstrated a notable reduction in PO_4-P leaching compared to mineral fertilizer.

Biochar incorporation into soil enhances nitrogen retention by adsorbing NH_4^+ onto its surface, reducing leaching losses and increasing its accessibility for plant uptake (Joseph et al., 2021).

However, LNF and LNFb biochars led to additional nitrogen runoff, exhibiting similar effects to NP_{min}. In contrast, Troy et al. (2014) demonstrated that incorporating biochar into soil amended with pig manure can effectively reduce nutrient leaching. Their study found that adding wood-derived biochar decreased nitrate and organic carbon leaching, highlighting its potential to enhance nutrient retention in agricultural soils. The higher nitrogen loss in LNF biochar-treated soils may be attributed to the influence of biochar on soil microbial activity, mineralization rates, and adsorption-desorption dynamics, as reported in previous studies (Verheijen et al., 2009; Sharma et al., 2025). At the same time, NF-based biochars did not cause any significant phosphorus or nitrogen losses when compared to the control, suggesting their potential to mitigate nutrient leaching after application into the soils.

Characteristics of biochar chemical stability. Biochar has emerged as a promising tool for carbon sequestration and climate change mitigation. Its potential to sequester carbon lies in its chemical stability. Therefore, understanding and enhancing the carbon stability of biochar is essential for maximizing its role in climate change mitigation strategies. FTIR analysis is a useful method for assessing carbon stability by evaluating surface functional groups (Adhikari et al., 2024).

As shown in the FTIR spectra of LNF, NF, and NFb (Figure 2), the vibrations of carbon chemical bonds produce high peak intensities across all three samples. The most pronounced peak intensity occurs around 1090 cm^{-1}, corresponding to the vibration of C–O bonds in cellulose- and hemicellulose-derived organic structures (this peak is absent in LNF).

The peak at 1425 cm^{-1} is attributed to C–C bond vibrations in hemicellulose structures, while peaks at 1650 cm^{-1} and 1740 cm^{-1} correspond to C=C and C=O bonds in lignin aromatic structures (these peaks exhibit weak intensity in NF). Additionally, the doublet peaks at 2800 cm^{-1} and 2900 cm^{-1} result from the presence of aliphatic carbon in CH_2 and CH_3 structures.

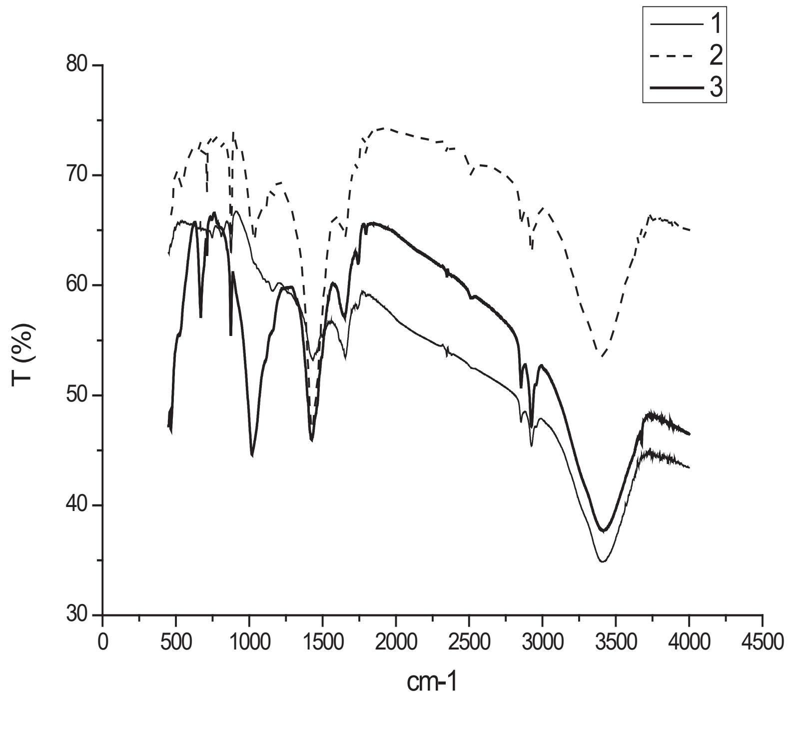

Figure 2. FTIR spectra of biochar samples: (1) LNF, (2) NF and (3) NFb

The FTIR spectral patterns of NF and NFb show close similarity, whereas LNF exhibits lower peak intensities, indicating a lower concentration of structural components. The highest peak intensity of carbon bonds and aromatic carbon in NFb suggests an important role of bentonite in the chemical stability of biochar.

CONCLUSIONS

Pyrolysis of LNF and NF resulted in distinct biochar properties, with NF producing higher yields, while LNF exhibited a higher surface area.

The incorporation of bentonite during pyrolysis significantly improved the biochar's surface area and pore volume, particularly in the mesopore range.

All biochars exhibited high sorption capacity for nitrogen and phosphorous when loaded with liquid manure, with bentonite-modified biochars showing more superior retention.

Nutrient-rich fiber biochars (NF and NFb) effectively reduce phosphorus leaching, making them promising amendments for sustainable soil management.

Biochar from low-nutrient fiber does not effectively retain nitrogen and may contribute to nitrogen losses comparable to mineral fertilizers.

FTIR analysis showed that biochar derived from nutrient fiber exhibited the highest peak intensity of carbon bonds, highlighting the positive effect of bentonite on biochar's carbon stability.

Further research is necessary to optimize pyrolysis conditions and assess the long-term impacts of these biochar treatments on soil health and nutrient cycling.

ACKNOWLEDGMENTS

This work was supported by the Finnish Natural Resources Research Foundation.

REFERENCES

Adhikari, S., Moon, E., Paz-Ferreiro, J., & Timms, W. (2024). Comparative analysis of biochar carbon stability methods and implications for carbon credits. *Science of The Total Environment, 914*, 169607. https://doi.org/10.1016/j.scitotenv.2023.169607

Atkinson, C. J., Fitzgerald, J. D., & Hipps, N. A. (2010). Potential mechanisms for achieving agricultural benefits from biochar application to temperate soils: A review. *Plant and Soil*, *337*(1-2), 1–18.

Beesley, L., Moreno-Jiménez, E., Gomez-Eyles, J. L., Harris, E., Robinson, B. & Sizmur, T. (2010). A review of biochar's potential role in the remediation, revegetation, and restoration of contaminated soils. *Environmental Pollution, 159*(12), 3269–3282. https://doi.org/10.1016/j.envpol.2011.07.023

Borchard, N., Schirrmann, M., Cayuela, M. L., Kammann, C., Wrage-Mönnig, N., Estavillo, J. M., Fuertes-Mendizábal, T., Sigua, G., Spokas, K., Ippolito, J. A., & Novak, J. (2019). Biochar, soil and land-use interactions that reduce nitrate leaching and N2O emissions: A meta-analysis. *Science of The Total Environment, 651*(2), 2354–2364. https://doi.org/10.1016/j.scitotenv.2018.10.060

Camberato, J. J., Gagnon, B., Angers, D. A., Chantigny, M. H., & Pan, W. L. (2006). Les sous-produits de papetières comme amendement pour les sols et sources d'éléments nutritifs pour les cultures. *Can. J. Soil Sci, 86,* 641–653.

Cao, X., Meng, Z., Song, E., Sun, X., Hu, X., Li, W., Liu, Z., Gao, S., & Song, B. (2022). Co-adsorption capabilities and mechanisms of bentonite enhanced sludge biochar for de-risking norfloxacin and Cu2+ contaminated water. *Chemosphere, 299*, 134414. https://doi.org/10.1016/j.chemosphere.2022.134414

Chatterjee, R., Sajjadi, B., Chen, W.-Y., Mattern, D. L., Hammer, N., Raman, V., & Dorris, A. (2020). Effect of pyrolysis temperature on physicochemical properties and acoustic-based amination of biochar for efficient CO_2 adsorption. *Frontiers in Energy Research, 8*. https://doi.org/10.3389/fenrg.2020.00085

Chen, L., Chen, X. L., Zhou, C. H., Yang, H. M., Ji, S. F., Tong, D. S., Zhong, Z. K., Yu, W. H., & Chu, M. Q. (2017). Environmental-friendly montmorillonite-biochar composites: Facile production and tunable adsorption-release of ammonium and phosphate. J. *Cleaner Prod*., *156,* 648–659. https://doi.org/10.1016/j.jclepro.2017.04.050

Dadrasnia, A., Muñoz, I. B., Yáñez, E. H., Lamkaddam, I. U., Mora, M., Ponsá, S., Ahmed, M., Argelaguet, L. L., Williams, P. M., & Oatley-Radcliffe, D. L. (2021). Sustainable nutrient recovery from animal manure: A review of current best practice technology and the potential for freeze concentration. *Journal of Cleaner Production*, *315*, 128106. https://doi.org/10.1016/j.jclepro.2021.128106

Hagemann, N., Spokas, K., Schmidt, H.-P., Kägi, R., Böhler, M., & Bucheli, T. D. (2018). Activated carbon, biochar and charcoal: Linkages and synergies across pyrogenic carbon's ABCs. *Water, 10*(2), 182. https://doi.org/10.3390/w10020182

Joseph, S., Cowie, A. L., van Zwieten, L., Bolan, N., Budai, A., & Buss, W. (2021). How biochar works, and when it doesn't: A review of mechanisms controlling soil and plant responses to biochar. *GCB Bioenergy*, *13*(1), 31–49. https://doi.org/10.1111/gcbb.12885

Kammann, C., Ippolito, J., Hagemann, N., Borchard, N., Cayuela, M. L., Estavillo, J. M., Fuertes-Mendizabal, T., … & Wrage-Mönnig, N. (2017). Biochar as a tool to reduce the agricultural greenhouse-gas burden? *GCB Bioenergy, 9*(6), 1081–1091. https://doi.org/10.3846/16486897.2017.1319375

Karod, M., Pollard, Z. A., Ahmad, M. T., Dou, G., Gao, L., & Goldfarb, J. L. (2022). Impact of Bentonite Clay on In Situ Pyrolysis vs. Hydrothermal Carbonization of Avocado Pit Biomass. *Catalysts*, *12*(6), 655. https://doi.org/10.3390/catal12060655

Laird, D. A., Fleming, P., Davis, D. D., Horton, R., Wang, B., & Karlen, D. L. (2010). Impact of biochar amendments on the quality of a typical Midwestern agricultural soil. *Geoderma, 158*(3-4), 443-449. https://doi.org/10.1016/j.geoderma.2010.05.013

Leng, L., Xiong, Q., Yang, L., Li, H., Zhou, Y., Zhang, W., Jiang, S., Li, H., & Huang, H. (2021). An overview on engineering the surface area and porosity of biochar. *Science of The Total Environment, 763*, 144204. https://doi.org/10.1016/j.scitotenv.2020.144204

Murphy, J., & Riley, J. P. (1962). A modified single solution method for the determination of phosphate in natural waters. *Analytica Chimica Acta*, *27*, 31–36. https://doi.org/10.1016/S0003-2670(00)88444-5

Munar-Florez, D. A., Varón-Cardenas, D. A., Ramírez-Contreras, N. E., & García-Núñez, J. A. (2021). Adsorption of ammonium and phosphates by biochar produced from oil palm shells: Effects of production conditions. *Results in Chemistry, 3*, 100119. https://doi.org/10.1016/j.rechem.2021.100119

Ortiz, L. R., Torres, E., Zalazar, D., Zhang, H., Rodriguez, R., & Mazza, G. (2021). Influence of pyrolysis temperature and bio-waste composition on biochar characteristics. *Renewable Energy*, *155*, 837–847. https://doi.org/10.1016/j.renene.2020.03.181

Reis, G. S. D., Bergna, D., Tuomikoski, S., Grimm, A., Lima, E. C., Thyrel, M., Skoglund, N., Lassi, U., & Larsson, S. H. (2022). Preparation and Characterization of Pulp and Paper Mill Sludge-Activated Biochars Using Alkaline Activation: A Box–Behnken Design Approach. *ACS Omega*, *7*(36), 32620–32630. https://doi.org/10.1021/acsomega.2c04290

Sharma, M., Kaushik, R., Pandit, M. K., Lee, Y.-H. (2025). Biochar-Induced Microbial Shifts: Advancing Soil Sustainability. *Sustainability, 17*(4), 1748. https://doi.org/10.3390/su17041748

Tomczyk, A., Sokołowska, Z., & Boguta, P. (2020). Biochar physicochemical properties: pyrolysis temperature and feedstock kind effects. *Rev Environ Sci Biotechnol, 19*, 191–215. https://doi.org/10.1007/s11157-020-09523-3

Troy, S., Richards, K. G., Healy, M. G., & Fenton, O. (2014). Biochar addition to soil reduces nitrate leaching from soil treated with pig manure. *Water, Air, & Soil Pollution*, *225*, 1900. https://doi.org/10.1007/s11270-014-1900-0

Turtola, E. (1996). Peroxodisulphate digestion and fi ltration as sources of inaccuracy in determinations of total phosphorus and dissolved orthophosphate phosphorus in water samples containing suspended soil particles. *Boreal Environment Research*, *1*, 12–26.

Uusitalo, R., Ylivainio, K., Hyväluoma, J., Rasa, K., Kaseva, J., Nylund, P., Pietola, L., & Turtola, E. (2012). The effects of gypsum on the transfer of phosphorus and other nutrients through clay soil monoliths. *Agricultural and Food Science*, *21*(3). 260–278. https://doi.org/10.23986/afsci.4855

Verheijen, F. G. A., Jeffery, S., Bastos, A. C., van der Velde, M., & Diafas, I. (2009). Biochar Application to Soils - A Critical Scientific Review of Effects on Soil Properties, Processes and Functions. Luxembourg: EUR 24099 EN, Office for the Official Publications of the European Communities, 149.

Wang, F., Zhang, R., Donne, S. W., Beyad, Y., Liu, X., Duan, X., Yang, T., Su, P., & Sun, H. (2022). Co-pyrolysis of wood chips and bentonite/kaolin: Influence of temperatures and minerals on characteristics and carbon sequestration potential of biochar. *Sci Total Environ*, *838*(2), 156081. https://doi.org/10.1016/j.scitotenv.2022.156081

Yao, Y., Gao, B., Zhang, M., Inyang, M., & Zimmerman, A.R. (2012). Effect of biochar amendment on sorption and leaching of nitrate, ammonium, and phosphate in a sandy soil. *Chemosphere, 89*(11), 1467–1471. https://doi.org/10.1016/j.chemosphere.2012.06.002

Yin, R., Wang, X., Li, S., & Zhu, L. (2018). Enhancing ammonium adsorption on biochar through oxygen-containing functional groups by air oxidation. *Science of the Total Environment, 616-617,* 995–1004. https://doi.org/10.1016/j.scitotenv.2017.10.203

Yuan, J. H. & Xu, R. K. (2011). The amelioration effects of low temperature biochar generated from nine crop residues on an acidic Ultisol. *Soil Use and Management*, *27*(1). 110-115. https://doi.org/10.1111/j.1475-2743.2010.00317.x

Zhang, M., Lin, K., Li, X., Wu, L., Yu, J., Cao, S., Zhang, D., Xu, L., Parikh, S. J., & Ok, Y. S. (2022). Removal of phosphate from water by paper mill sludge biochar. *Environmental Pollution, 293,* 118521. https://doi.org/10.1016/j.envpol.2021.118521

***European Union (2019). Regulation (EU) 2019/1009 of the European Parliament and of the Council of 5 June 2019 laying down rules on the making available on the market of EU fertilising products and amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009 and repealing Regulation (EC) No 2003/2003. *Official Journal of the European Union,* L170, 1–114. Available at: https://eur-lex.europa.eu/eli/reg/2019/1009/oj.