

BIOCHAR MICRONIZATION AND MATERIAL APPLICATIONS

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Key Words: Biochar, micronization, particle size, material applications, bio fly ash

Biochar is used in different applications; most commonly it is applied as land enhancement. Biochar is an environmentally friendly, carbon-negative biomaterial, which contributes to bio and circular economy. In South-Eastern Finland University of Applied Sciences (later Xamk) biochar is studied in BioSampo, a Research Centre for Bio and Circular Economy. Pyrolysis of different biomaterials has been one of the focus areas so far. In the near future biochar from different origins will also be micronized. Reduced particle size has many well-known advantages, such as increased surface area and reactivity. Therefore, micronization can enhance the utilization possibilities of biochar in different technical applications, for instance as a raw material in paint or filters. After the micronization tests have been carried out in BioSampo, the best applications will be evaluated. For this evaluation, particle size distributions of micronized biochar will be analysed. This information is also crucial for the further development of the micronization process. As results of the micronization tests and the evaluations, the most potential applications are identified and recommendations for future actions considering micronized biochar are given. Xamk has a long history in the micronization of ash, mostly bio fly ash. Currently there are pilot-scale opposed jet mill micronization equipment in BioSampo. This equipment can also be used in classification. In the micronization process, the material is fed into the system, where it is ground in one or two opposed jet mills and classified into two fractions. The micronization of biochar will differ from that of bio fly ash at least in one significant way – biochar dust can be explosive. Thus, the micronization process requires an inert atmosphere, which prevents carbon from igniting. These issues are addressed in a project called “Biochar and bio fly ash micronization and material applications in Kymenlaakso region”, in short “HITU”. During the project bio fly ash from several power plants has been micronized. Two of the most potential, micronized ashes have been tested in concrete for compressive strength. The aim of these experiments is to enhance the utilization of bio fly ash and to decrease the need for natural resources in concrete. HITU is administrated by Xamk and the project duration is 1.8.2018 – 31.12.2020. The main funder is the European Regional Development Fund (ERDF). For more information and contact info, see www.xamk.fi/hitu-en and www.xamk.fi/en/biosampo.



Figure 1 – Pre-treated BioChar in BioSampo (Picture: Manu Eloaho)

THE POTENTIAL FOR BIOCHAR TO MITIGATE THE IMPACT OF CLIMATE CHANGE

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Key Words: Biochar, Mesocosms, Climate Change, Water Retention, Arid Soil

The United Arab Emirates produces over 44 million date palm trees yearly, where date palm is mainly used as source of food and shelter. Each tree generates approximately 20 Kilograms of palm frond waste per year and this waste is currently sent to landfills. In this study, we proposed that in the arid climate and soil conditions found in the UAE, this date palm waste could be converted to biochar and used to improve the water holding capacity of UAE soils. Therefore, the aim of this study was to test whether amendments of date palm frond (DPF) and its biochar could improve the water holding capacity of soils. A mesocosm design and a plant growth experiment were used in the laboratory to assess the treatments under UAE summer temperature conditions. For the mesocosm, there were 6 different biochar and DPF treatments (1%, 3%, 6%, 12%, 15% and 18% biochar or DPF in soil) along with the controls (sharp sand, DPF biochar and DPF). The experiment was divided into 3 cycles (wet, dry, and dry without water bowl (wow)). The impact of the experimental treatments was assessed using ANOVA. Both Biochar and DPF had no significant effect during the first two cycles (wet and dry) but during the third cycle, the DPF appeared to have better water holding capacity than Biochar. A plant growth experiment was conducted with 6 different treatment (controls - sand, DPF and Biochar; and Biochar at 1%, 6% and 15%). Cat grass was used as a quick growing crop with its height and leaf area monitored while the soil was monitored for its moisture and pH. Water was irrigated during the first 3 weeks then the soil treatments left to dry. The results show the greatest growth for 1% Biochar. The processes are being investigated using thermal gravimetric analysis (TGA) to assess water binding capacity and strength of the Biochar, DPF and soil.

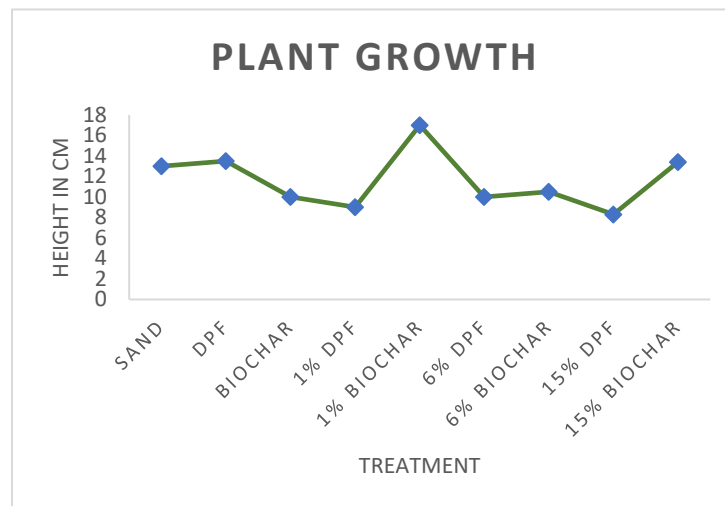


Figure 1 – Plant growth results showing the 1% Biochar is the highest growth

EFFECT OF BIOCHAR ADDITION TO METAL-CONTAMINATED SOIL ON *PHASEOLUS VULGARIS*

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Key Words: *Phaseolus vulgaris*, metal contamination, pig manure-derived biochar

The soil of the Campine region in Belgium is polluted with metals such as cadmium (Cd), copper (Cu) and zinc (Zn) due to past industrialization (Schreurs *et al.*, 2011). When this soil is used for agriculture, these metals can accumulate in crops and cattle. To enlarge the available land to produce safe crops with high productivity, addition of biochar to the soil is considered a possible solution. Biochar has been proven to possess many advantages. When added to the soil, it can adsorb metals like Cd and hence reduce its bioavailability for plants (Li *et al.*, 2017). Pig manure is an interesting feedstock to pyrolyze into biochar because it is highly abundant in Belgium. To investigate the capability of this biochar type, pot experiments were performed to study the effect of biochar addition to polluted soil on *Phaseolus vulgaris*. The environmental norms of the Flemish government indicate the safe and allowed quantity ($\text{mg}\cdot\text{kg}^{-1}$ dry matter) of metals in a reference soil (10% clay, 2% organic matter). A metal-contaminated soil exceeding these guidelines for Cd, Cu and Zn for at least eighty percent was mixed with 0%, 1% or 2% pig manure-derived biochar. On the one hand, this experiment showed that the biomass of *P. vulgaris* (stems, leaves and beans) was dose-dependently enhanced by biochar application. On the other hand, metal determination in beans and leaves showed an opposite relation, mainly a biochar-related decrease in metal concentration. The latter was in most cases reflected in higher remains of metals in the soil. In conclusion, *P. vulgaris* grown on metal-contaminated soil mixed with pig manure-derived biochar showed a higher crop yield than plants without biochar. This enhanced growth seemed to be dose-dependent within the concentration range tested, but this should be further researched in other plant species and substrates. In addition, pig manure-derived biochar diminished the translocation of Cd, Cu and Zn to the aboveground parts of the plant. These results indicate that pig manure-derived biochar could be used to enhance the growth of crops and diminish the uptake and accumulation of metals, although further research on other feedstock-derived biochar is necessary.

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EFFECT OF BIOCHAR AMENDMENT ON NUTRIENT FLUXES DURING MANURE FERMENTATION

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Key Words: nitrogen, mineralization, activation, greenhouse gas emissions

Biochar is a charred organic matter often used as a soil amendment. Among other beneficial applications in agriculture belongs to its usage as an additive and bulking agent in composting. The biochar amendment to manure has the potential to reduce greenhouse gas emissions and nutrient leaching during the composting process. Biochar addition reduces NH_3 and N_2O emissions from manure. Recent studies showed that maximal ammonium sorption occurs on low pyrolysis temperature (400 °C) biochar at near neutral pH (7.0–7.5). Consequential lower NH_3 emission is explained due to the greater incorporation of ammonium (NH_4^+) in organic compounds during microbial utilization of dissolved organic carbon (DOC). Both facts are related to findings that low-temperature biochar have a much higher content of utilizable carbon as well as less low molecular weight (LMW) acids. However, the knowledge of the impact of biochar on the mineralization of manure is still sparse. More studies about the effects of biochar on both nitrification and denitrification processes during composting are needed.

The main interest of our studies was the transformation of organic nitrogen during the fermentation process of biochar-amended manure. A small-scale FYM- experiment for monitoring the fermentation of FYM amended by various amounts of biochar was designed and carried out in 50 liters tightly closed barrels. Each of these barrels was filled up with 20 kg of FYM, biochar was added in some barrels in amounts corresponding to particular variants. All variants were prepared in five replicates. The experimental variants were as follows: [1] control FYM; [2] FYM + biochar 40 g.kg⁻¹; [3] FYM + biochar 100 g.kg⁻¹; [4] FYM + biochar 200 g.kg⁻¹. The portion of 17 g of biochar closed in a polyurethane bag was inserted in each barrel containing biochar as a control sorption matrix for monitoring of time-course microbial and chemical enrichment of biochar. These biochar samples served also for monitoring of changes in surface structure and chemical parameters. The fermentation process was run for 6 weeks on a shaded place (stables), a concentration of NH_4^+ was periodically measured. FYM was sampled at time 0, 13, 27, and 41 days from the start of the experiment. pH values and the dry mass were estimated, chemical analyses of nutrients (N, P, K) were done. Microbial biomass was quantified via qPCR SYBR-green methods for estimation of: 16S rDNA copy number (bacteria), 18S rDNA (fungi), amoA gene copy number (ammonium oxidizing bacteria - AOB).

The results showed that amoA copy number and concentration of NH_4^+ changes indirectly to the increasing amount of amended biochar whereas the nitrogen content is comparable between all variants. Differences in amounts of bacteria, *Actinomycetes*, and fungi may indicate biochar-mediated changes in utilization of nutrient sources and in mineralization of organic nitrogen and carbon. The abundance of methanogenic microflora (quantified by qPCR) significantly increased during the fermentation process but possible methane formation was putatively mitigated by the addition of biochar, thus the variants amended with high amount of biochar exerted lower methanogen-specific 16S rDNA values.

The FYM-biochar fermentation technology is intended to produce superior quality FYM type fertilizer enriched with nutrients (thus reduced production of greenhouse gases should protect nutrition elements from volatilization) and to produce beneficial soil amendment biochar, which might be activated by structural changes mediated during the FYM fermentation via the activity of microorganisms. Thus, the aim of ongoing study is also the development of an efficient method for the bio-activation of biochar.

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TESTING BIOCHAR AS SORBENT TO DECREASE SAMARIUM MOBILITY IN CONTAMINATED AREAS

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Key Words: Biochar, Coal fines, Sorption, Desorption, Samarium

Samarium (Sm), a rare earth element of lanthanides group, is an emerging contaminant that has been found in wastes resulting from agricultural and industrial activities, especially in China. There are many evidences of watersheds that, due to contamination by industrial wastes, specially mine tailings, contain Sm at high concentration levels, such as the case of Baotou Area containing up to $130 \mu\text{g Sm L}^{-1}$ (1). Besides, some works have also reported that the Sm concentration in lands treated with rare earth-rich fertilizers or irrigated by the abovementioned contaminated water sources is abnormally high, e.g., 492 mg kg^{-1} in Bayan Obo (2). This concomitant soil contamination is also of special concern since soils can act as sink of Sm that can be further incorporated in the food chain or reintroduced into water sources due to irrigation and raining processes. Biochars are increasingly being considered as sorbents for the removal of inorganic pollutants from contaminated waters (Doumer, 2016), but also as soil amendments as they may have a high sorption capacity for several inorganic pollutants, and they are also low-cost materials that may improve soil properties as water holding capacity, nutrient status and pH. However, secondary effects on soil solution composition, as the increase in the dissolved organic carbon (DOC), jeopardize their application for several pollutants, such as heavy metals forming soluble chelates with organic matter compounds. Moreover, biochar will decrease contaminant mobility in soils only when the sorption capacity of biochar exceed that of the soil in various orders of magnitude, considering the low dose (often lower than 10% w/w) with which they will be applied. Therefore, laboratory assays are required to assess the sorption properties of a biochar before using it at field level as soil amendment or as sorbent for water filtration. In the case of lanthanides, there are scarce data on their mobility in soils and on their sorption by biochars. In this work, we examine the capacity of a set of biochars of varying pH and DOC, to sorb Sm, as representative for lanthanide pollutants, in a wide range of Sm concentrations. Biochar concentration-dependent sorption capacities were compared with those of activated charcoal and of a by-product from the metallurgical industry (coal fines). Results indicated high sorption capacities at low Sm concentration range (up to distribution coefficients of 10^4 L/kg), with desorption rates lower than 1%. Distribution coefficients of Sm in biochar significantly decreased when increasing Sm concentration levels, indicating saturation of the sorption sites of the material with maximum sorption values very similar to the cation exchange capacity of the biochar and suggesting that the main interaction mechanism was cation exchange. The implications of the use of biochars in soil remediation actions as well as in the treatment of contaminated waters are also discussed.

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FACTORS AFFECTING THE SORPTION OF PERFLUOROALKYL SUBSTANCES IN BIOCHARS AND OTHER CARBON-RICH BYPRODUCTS

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Key Words: Biochar, Carbon-rich byproducts, Sorption, Desorption, Perfluoroalkyl Substances

Biochar is the solid byproduct obtained after the pyrolysis process of biomass waste, and it is usually applied in agricultural soils to increase soil organic carbon, and improve soil structure and water retention, among other benefits. As long as it has been demonstrated that biochar successfully sorbs either organic and inorganic pollutants, the investigation of other potential applications, such as water remediation, are of increasing interest (1). Similarly, other carbon-rich byproducts such as compost or coal fines are supposed to have similar properties than biochar. In this study, the sorption properties of biochars of different characteristics have been investigated and compared with those of other carbon-rich materials. As target compounds, we have used perfluoroalkyl substances (PFASs), which are pollutants of concern because of their high bioaccumulation, extreme persistence and toxic properties, and widespread in different environmental compartments, among them soils and waters (2). Sorption parameters of seven PFASs with different perfluorinated chain length have been determined in biochar, compost and coal fines, using batch experiments according to the OECD 106 guidelines. Biochars of different biomass wastes were obtained by slow pyrolysis at 350°C and a rate of 5°C min⁻¹, achieving biochar yields between 40% and 90% depending on the feedstock (3). The effect of various experimental conditions (contact time, initial PFASs concentration, pH and composition of contact solution) in the sorption capacity of the materials was evaluated. Sorption was slightly faster for the long-chain PFASs, with more than 90% of sorption of PFNA in 24 h in all materials. For longer times, in almost all materials, a 100% of sorption was reached. Linear isotherms were obtained for all the PFASs in all materials in a wide range of concentrations, allowing the calculation of a solid-liquid distribution coefficient (K_d) and a solid-liquid distribution coefficient referred to the organic carbon of the material (K_{oc}) for every PFAS-material combination. Similarly, in a previous work (4), linear isotherms were also obtained for the same PFASs in soils, using similar experimental conditions. The sorption process in all matrices was considerably irreversible, especially for the long chain PFASs. The obtained log K_{oc} values for each PFAS in each material were successfully correlated with the number of CF₂ units of the alkyl chain and the log K_{ow} values of the PFASs, which suggest that hydrophobic interaction is the main mechanism controlling PFASs sorption in biochar and other carbon-rich materials. Moreover, the sorption of PFASs in the materials was negatively correlated with the dissolved organic carbon (DOC) of the aqueous solution, which was attributed to a competitive sorption process of PFASs with the dissolved organic matter. Therefore, materials with low DOC, as is the case of most biochars, are the best candidates for PFASs sorption. Low pH values and high cationic content of the aqueous solution also contribute to a decrease of DOC and, therefore, leads to optimum PFASs sorption in the material.

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CHARACTERIZATION OF TREE BARK BIOCHAR AND EVALUATION OF ITS POTENTIAL TO USE IN HORTICULTURAL GROWING MEDIUMS

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Key Words: Bark biochar, Horticultural growing mediums, Seed germination assay, Nutrient dynamics.

Peat is popular in horticulture industry as a main constituent in the horticultural growing medium due to its high water holding capacity, improve aeration in the medium, ability to adjust the pH and fertility level in the substrate as required and pathogen freeness. However, the use of peat in growing mediums cause for the environmental problems such as greenhouse gas emissions due to excavating and drainage of natural peatlands. As a sustainable approach and an alternative to peat, biochar is getting attention due to its stable nature. As a byproduct of pyrolysis, biochar has high porosity, high pH, high cation exchange capacity (CEC) and high water holding capacity. These properties make biochar as an appropriate constitute in growing medium applications with long term plant productivity. Within this context, the aim of this study was to examine the potential of biochar produced from bark as an alternative to peat use in growing mediums. Biochar was characterized for elemental, proximate, organic matter content, pH, EC, Py GC-MS and FT-IR. Then, five growing medium substrates including peat only, biochar only, biochar and peat in 1:1, 1:3, 3:1 (V/V) ratios were analyzed for pH, electrical conductivity (EC), CEC, bulk density, porosity, water holding capacity, aeration, and particle size distribution parameters. Germination test was carried out to assess the phytotoxicity of the formulated substrates. Preliminary plant growth test was carried out to determine the tomato seedling growth up to four weeks. Additionally, one month of laboratory incubation was conducted to determine the pore water nutrient dynamics. For that, nitrate-N, phosphate-P and sulphate-S in rhizone extractions in each growing medium formulations were collected weekly up to one month of period. Addition of biochar into peat increased the pH, EC, and CEC of all peat and biochar mixed treatments. According to the germination test results for the cress, lettuce and tomato seeds, the addition of biochar into peat had significantly increased the germination percentage, shoot and root length of the germinated seeds compared to the peat only treatment. Addition of bark biochar into peat significantly increased the plant growth parameters compared to peat only and biochar only treatments. Nitrate-N, sulphate-S and phosphate-P content in pore water of each substrate were significantly high in biochar added treatments compared to the peat only treatment. These results indicate that bark biochar could use to partially replace peat use in horticultural growing mediums.

CHEMICAL STABILIZATION OF Cd CONTAMINATED SOIL USING FRESH AND AGED WHEAT STRAW BIOCHAR

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Key Words: Biochar, Wheat straw, Accelerated aging, heavy metal immobilization, Biochar stability

Soil pollution can adversely affect the ecosystem services provided by the soil. Polluted soils reduce land productivity by reducing crop yields and polluting groundwater. Also, both crops and water in polluted lands may be unsafe for the consumption by animals or humans. Release of chemicals or toxic substances can happen through industrial and agricultural activities. Metal mining and smelting to separate minerals is one such activity which can introduce large quantities of heavy metals into the environment which persist in the soil for long periods even after those activities are ended. The Campine area on the border of Belgium and the Netherlands contains Cd contaminated sites due to historic metal smelting activities. A soil collected in that region containing 11 ± 0.5 ppm Cd exceeding soil remediation standards was taken in consideration for this soil remediation study. Biochar is increasingly getting attention as a remediation tool to immobilizing heavy metals in contaminated soils. However, long-term provisioning of such service is mainly dependent on the biochar carbon stability. Biochar carbon stability is mainly dependent on the biochar production conditions, nature of the feedstock material and the biotic and abiotic environmental conditions that biochar is being used. Also, the heavy metal immobilization process heavily depends on the soil and biochar pH and the nature of the functional groups present on biochar surfaces such as carbonates and phosphates. Within this context, three types of wheat straw biochar were produced using a screw reactor at 400 °C, 500 °C, and 600 °C. To age the biochar samples, biochar samples were subjected to accelerated aging using a method suggested by Cross and Sohi, 2013 [1]. This method can be used as a proxy for environmental aging of biochar approximately 100 years under temperate conditions. Then these six biochar samples (BC_{400F}, BC_{500F}, BC_{600F}, BC_{400A}, BC_{500A}, BC_{600A}) were characterized for elemental analysis, ash content, volatile matter content and fixed carbon content, pH, EC, phosphate and carbonate content and FT-IR analysis. The soil used in this study was characterized for the soil texture, elemental contents, organic matter content, pH and EC. Six months of laboratory incubation study was conducted with contaminated soil amended with each type of biochar at 2 % rate (w/w). Rhizon extractions were collected at the end of each month to quantify the Cd concentration, pH and total organic carbon content in the soil pore water. At the end of the six months of incubation time, Cd concentration in the pore water ranged from 100.36 ppb in BC_{600A} to 249.85 ppb in BC_{400A}. The Cd concentration in each treatment was BC_{600A} < BC_{400F} < BC_{600F} < BC_{500F} < Soil only (control) < BC_{500A} < BC_{400A}. According to the FT-IR analysis of the six biochar samples, more carboxylic-C and carbonate-C functional groups were present in aged biochar samples compared to the freshly produced wheat straw biochar samples. Also, biochar produced at lower temperatures were characterized by lower pH and a lower amount of stable C compounds compared to the biochar produced freshly and in higher production temperatures. These results suggest that the stability of biochar carbon and pH of both biochar and soil have a significant impact on the stabilization of heavy metals in the soil environment. Therefore, the selection of biochar with desired qualities thus choosing of suitable biochar production conditions is essential in decision-making processes to keeping the biochar services in the long run.

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PRODUCTION AND CHARACTERIZATION OF BIOCHAR PRODUCED FROM CO-PYROLYSIS OF LIGNOCELLULOSIC BIOMASS AND PLASTIC MULCHING SHEETS

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Key Words: Agricultural plastic, Low density polyethylene, copyrolysis, analytical pyrolysis, biochar

Agricultural biomass waste contaminated with agricultural plastics is a prominent waste stream in intense agricultural areas and complete separation of the plastic residues from the biomass is not always straightforward. There is a high possibility to use agricultural biomass and agricultural plastic wastes together in a single stream to produce valuable products via pyrolysis. However, effect of small scale plastic material presence on pyrolysis product yield is still unknown. Hence, the effect of low levels of agricultural plastics in the biomass on the mass balance and product composition of pyrolysis products were examined during this study. Co-pyrolysis of mixed soft wood and low-density polyethylene (black color agricultural plastic used for mulching) was carried out at 500 °C in a mini pyrolysis reactor set up. The produced char was characterized using proximate, elemental analysis, thermogravimetric analysis and analytical pyrolysis at 750 °C using PyGC/MS. Five types of char were produced during this study. Namely soft wood only (0%AgPIC) and mixtures of 1%, 5%, 10%, and 25% agricultural plastic material and soft wood (mass basis), referred to as 1%AgPIC, 5%AgPIC, 10%AgPIC and 25%AgPIC respectively. According to the mass balances experimentally obtained, the char yield was not significantly altered after incorporation of the plastic material into the feedstock. However increased plastic mass fraction increased the yield in tar/oil and decreased the gas yield. Moreover, the fixed C content and total C content were reduced and volatile matter content, total H content and H/C molar ratio were increased in the char material with increased levels of plastic in the feedstock. This indicates the lower stability of char produced with higher plastic levels. According to the analytical pyrolysis results of the char, molecular compounds composition was varying after plastic material incorporation. Phenol, toluene and xylene peak area percentage were higher in plastic incorporated char materials. These results can be used to understand the biomass and plastic interaction during pyrolysis. Further studies are recommended to identify the contaminants in the products of copyrolysis of agricultural biomass feedstocks contaminated with plastics.

PRACTICAL ASSESSMENT OF BIOCHAR STABILITY INDICATORS: SENSITIVITY TO FEEDSTOCK TYPE AND PRODUCTION CONDITIONS

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Key Words: Biochar, Stability determination, Pyrolysis, Edinburgh stability tool, Analytical pyrolysis

Addition of biochar to soil, among other beneficial abilities has the potential of the carbon sequestration, improvement of soil fertility, and remediation of contaminated land (e.g., heavy metals immobilization). In a long-term perspective, these positive properties depend on the resistance against decomposition (stability) of the biochar in the soil matrix. The stability is influenced by the biochar production process parameters (i.e., pyrolysis), feedstock's origin, and the (a)biotic environmental conditions [1]. Due to numerous factors impacting on the stability, its objective assessment is a complex task, and one assessment method can be not sufficient. In literature has been reported several biochar stability indicators, but each of them rather covers the influence of the specific factor, than give complete information of biochar's stability. Therefore is legitimate to ask the question, are the stability predictors show any similarities between each other? An investigation of possible correlations among results from different stability assessment methods can lead to the improvement of the understanding of the biochars stability, and development of one, objective assessment's method. [2]. In this study, were analyzed 24 biochar samples produced from a variety of the feedstock: algal biomass, agricultural residues and wastes, woody biomass, and industrial wastes. Highest treatment temperature (HTT) during pyrolysis ranged from 300 °C to 750 °C with a residence time of the materials from 10 to 90 minutes and the heating rate from 5 to 25 °C/min. For the indicators similarity assessment, the stability indicators were derived, among others: H/C ratio, recalcitrance index (R_{50}), stability according to the Edinburgh stability tool (EST) [2], compounds ratios from analytical pyrolysis measurement (e.g., benzene/toluene ratio). The Principal Component Analysis (PCA) was performed to grasp possible trends in this high-dimensional data. Two main principal components (i.e., dimensions) of PCA retained ca. 70% of the original variance in the data, which is satisfactory value, especially for such inhomogeneous data matrix. Results arrangement indicated that the first principal component (PC1) could be strongly linked with the biochar's stability, and the second component (PC2) can be related to the biochar's feedstock origin. The H/C ratio, VM content (d.b.), benzene/toluene ratio, the EST and the R_{50} shown the highest impact on the first component and were assumed as the feedstock-independent biochar's stability indicators. The FC and ash content (d.b.), O/C ratio, phenol/benzene ratio were shown the highest impact on PC2. Therefore, they were assumed as the feedstock-dependent parameters. Since the feedstock properties are usually treated as unchangeable parameters, the correlations between the feedstock-independent, so production-dependent predictors were investigated. The H/C ratio shown a good Pearson correlation with benzene/toluene ratio (-0.76) and a bit weaker with EST (-0.61). The benzene/toluene ratio was shown correlation with R_{50} index (0.56) and EST (0.67). In conclusion, successful division of the stability indicators on the feedstock-dependable and -independent was achieved. It allowed observing a correlation between pairs of stability indicators. Therefore the existence of the similarities between certain parameters was proven. Future analysis of the data should focus on the ruling out possible multicollinearity in the stability indicators dataset. It will allow minimizing and clear the dataset for the objective stability assessment. That can open the route for establishing one, multipart stability parameter, which can be beneficial in biochar stability improvement studies and allow for broader application of the biochar in the future.

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POINT OF ZERO CHARGE DETERMINATION OF TEN STANDARD BIOCHARS FOR THE REMOVAL OF METHYLENE BLUE FROM AQUEOUS SOLUTIONS

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Key Words: biochar, point of zero charge, salt addition, methylene blue, adsorption.

This study describes the determination of the point of zero charge (PZC) of ten standard biochars (BC), supplied by the UK Biochar Research Centre (UKBRC), using the salt addition method, in order to select suitable biochar(s) for methylene blue removal from aqueous solutions. The initial pH (pH_i) was adjusted in a range of 3 to 13 using NaOH and HNO₃ solutions. The experiments employed a biochar dose of 10 g L⁻¹. The final pH values (pH_f) were recorded in the remaining suspensions after a 24-hour contact time at 120 rpm. The difference between pH_i and pH_f (ΔpH) was plotted against pH_i values and the pH at PZC (pH_{PZC}) corresponded to the point of intersection in the resulting curve. The results obtained in 0.1 mol L⁻¹ NaNO₃ were the following: PZC at 7.24 and 8.53 for rice husk biochar (RH), the first obtained at 550 °C pyrolytic temperature and the latter at 700 °C (RH550 and RH700); PZC at 8.81 and 9.46 for oil seed rape straw pellets biochar obtained at 550 °C and 700 °C (OSR550 and OSR700), respectively; PZC at 9.24 and 9.84 for wheat straw pellets biochar (WS550 and WS700, respectively); PZC at 8.98 and 8.94 for *Miscanthus* straw pellets biochar (MSP550 and MSP700, respectively); and PZC at 6.73 and 7.15 for soft wood pellets biochar (SWP550 and SWP700, respectively).

Table 1 – PZC values of the ten biochars

BC550	PZC	BC700	PZC
RH550	7.24	RH700	8.53
OSR550	8.81	OSR700	9.46
WS550	9.24	WS700	9.84
MSP550	8.98	MSP700	8.94
SWP550	6.73	SWP700	7.15

The pyrolytic temperature didn't influence the pH values at PZC for MSP biochar. The biochars that presented the lower PZC values are compatible with cationic dyes, such as methylene blue, because the pH of the solution can be easily adjusted to be higher than the pH at the PZC. When the $pH > pH_{PZC}$, the biochar's surface is negatively charged, favoring the adsorption of cations. Therefore, the most suitable biochars for which it would be easier to adjust the solution pH above the PZC would be RH550 (PZC = 7.24), SWP550 (PZC = 6.73) and SWP700 (PZC = 7.15).

On the other hand, the other biochars that achieved higher PZC values can be applied to anionic dyes adsorption, since the biochars' surfaces would be positively charged when the solutions' pH values were adjusted to below each biochar's PZC values. A preliminary study was conducted in order to evaluate the adsorption efficiency of RH550, SWP550 and SWP700 as adsorbents for methylene blue. The experiments were conducted for a 50 mg L⁻¹ methylene blue initial concentration, prepared as a solution at pH 8.

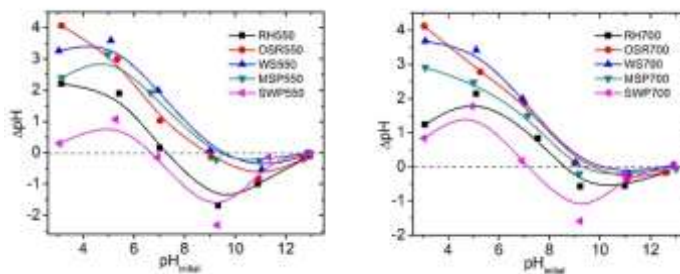


Figure 1 – PZC graphs for RH, OSR, WS, MSP and SWP.

This solution was placed in contact with each biochar in a dosage of 0.8 g L⁻¹ and 120 rpm during 2 hours. After that, the remaining methylene blue in solution was measured by UV-Vis, with maximum absorption at 668 nm. The removal efficiency calculated for methylene blue was of 66% for RH550, 26% for SWP550 and 20% for SWP700. Under the given conditions, RH550 biochar performed better as an adsorbent for methylene blue. However, more studies will be conducted and the effect of the adsorption parameters will be evaluated.

BIOCHAR ACTIVATED BY NUTRIENT- AND MICROORGANISMS-ENRICHED LIQUIDS AS A SOIL AMENDMENT

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Key Words: Biochar, Activation, Dehydrogenase activity, amoA gene (Ammonium Monooxygenase).

Biochar is very stable in nature and lasts for thousands of years. Biochar addition to soil positively affects the ecosystem, such as soil fertility and biological activity. Adding biochar to soil do not always increases soil activity. Studies have shown that biochar may also have a negative impact on soil microflora. Although biochar provides nutrients and mineralizable carbon to soil microorganism, due to its strong adsorption power, it pulls out soil nutrients away from the soil and may show a negative effect on soil microflora and rhizosphere. Modification of biochar is important to avoid its adverse effects. Physical and chemical modifications are a common method for the activation of biochar. Chemical modification has more advantage than a physical modification in term of porosity, greater surface area, less aromatic compound, and more oxygen-containing group. Chemical modification of biochar requires the use of strong chemicals which increase the risk to environment pollution. In the modern time with the increasing pollution, there is a demand for a low-cost green method to activate biochar, beneficial to the farmers and the environment. Uncommon biological activation of biochar fits in all the above aspects.

The specific aim of this study is to develop a low-cost and more environment-friendly method for activation of biochar. For the study, biochar prepared from plant residues was used for activation. Two weeks bathing of biochar was done in liquid enriched with nutrients and beneficial microorganisms. 15 gram of biochar was taken in a sealed polyurethane bag and dipped in each beaker containing nutrients enriched activation liquid and also in a beaker containing distilled water as a control. The variants of the experiment according to a type of used liquid were: [1] Distilled water (non-activated), [2] Medium M9, [3] M9 + Rewital Biogen Pro+ (commercial concentrate of helper soil and plant microorganisms). The activation liquid variant [2] Medium M9, contains dextrose as carbon source, Ammonium chloride (nitrogen), phosphate (phosphorus), sulfur, potassium, and magnesium. The activation liquid of variant [3] was prepared by inoculating medium M9 with Rewital Biogen Pro+ and incubated for three days at room temperature and under intense exposure to air. The activation liquids in a 500-ml bottle were aerated for 14 days at room temperature. Values of pH and glucose concentration were measured at the beginning and the end of the activation.

Activated biochar was tested as a soil amendment for its beneficial microbial enrichment in a pot plant growth experiment with lettuce (*Lactuca sativa*) seedlings. Activated biochar of all three variants was amended to the soil, negative control without biochar amendment was also prepared, sowed with lettuce seeds and grown under white light (20 000 lux) in phytotron (a 12 h photoperiod, temperature 18/22 °C (night/day), relative humidity 70%). After 42-days growth, the plants were harvested, the biomass of plants from all variants compared, and the biological parameters of soil at the beginning and the end of the experiment compared. Biological parameter compared were microbial biomass carbon (MBC), soil dehydrogenase activity (DHA) and soil microbial community abundance was determined by 16S rDNA (bacteria) and 18S rDNA (fungi), amoA gene (ammonium monooxygenase), nxr gene (nitrite oxidoreductase) and nirS gene (nitrite reductase).

From the overall result, it can be concluded that the number of bacteria, fungi, and values of microbial carbon and dehydrogenase activity in soil samples of all variants were comparable. The biomass of harvested lettuce seedlings does not show a significant difference. However, a significant increase (more than 2-fold) in the amoA gene were found for soil samples treated with variant [3] .

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GREEN AND NON-MECHANICAL METHOD FOR PRODUCTION OF COLLOIDAL-SIZE BIOCHAR FROM AGRICULTURE WASTE

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Key Words: Colloidal Biochar, Soil amendment, Sonicator.

Soil is an important source of nutrient and habitat to microflora. During the past 40 years', the world has lost one-third of its arable land due to an increase in the human population, excessive use of chemical fertilizers, and erosion. There is an urgent need to maintain sustainable approaches in agriculture system. Application of biochar as a soil amendment is a promising approach to improve soil physical, chemical, biological, and hydrological properties. In recent year's special attention has been focused on pyrolysis condition of biomass, although properties can also be enhanced by the reduction in particle size. Small-size biochar attracts increasing interest due to its unique environmental behavior. This research presents a physical method to modify biochar by ultrasonic radiation to produce colloidal size biochar. Agriculture waste biochar (1 cm) was used as a starting material. We used Malvern sonicator "Hydro 2000MU" of 20Hz frequency. Biochar (5gram) was added to 100 ml of deionized water and sonicated for 5 hr; after every 15 min of run time, sonicator was stopped for the next 15 min.

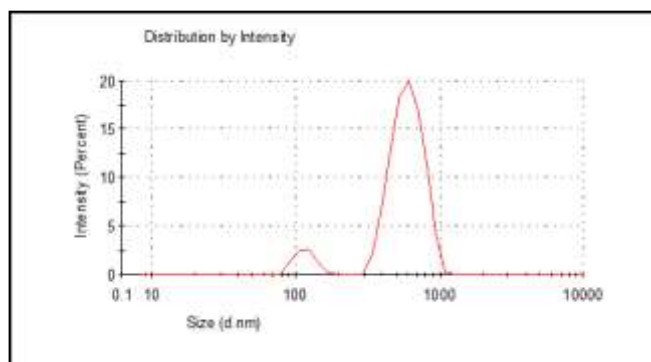


Figure 1. Size distribution by volume

Dynamic light scattering method (DLS) was used to measure the average size distribution of biochar particle. The volume-based particle size distribution of the biochar sample is illustrated in Fig. 1. DLS data showed a bimodal distribution. Two different peaks in nano and colloidal range were observed respectively. According to the histogram, more than 90% of particles were in the range of 400-1000nm. The zeta potential of biochar after sonication was -6.80, shows the stability of colloidal particles.

The produced colloidal-biochar was characterized by, Fourier transform infrared spectroscopy (FTIR) scanning electron microscopy (SEM). Some physical and chemical properties were also analyzed before and after sonication. (like water-holding capacity, elemental composition, polycyclic aromatic hydrocarbons (PAHs), organic matter). The adsorption test was performed to check the adsorption power of colloidal size biochar in removing harmful pollutants. Results confirm that colloidal size biochar is capable of removing micropollutants (carbamazepine) from aqueous medium. Result also confirm that there were no compositional and structural changes in biochar after sonication. We confirm that our method for the production of colloidal size biochar is green, robust and simple, however, more investigation is needed to reduce the particle size up to the range of 100nm.

IMMOBILIZATION OF HEAVY METALS BY MICROWAVE TORREFACTION OF SEWAGE SLUDGE WITH ADDITIVES

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Key Words: Sewage sludge; microwave torrefaction; biochar; immobilization of heavy metals.

The treatment of sewage sludge (SS) is one of the most important issues of the circular economy strategy in the European Union and in the Czech Republic (CR). New legislation in the CR strictly regulates the SS landfilling and its direct application in agriculture. One of the most important limiting factors for the use of SS in agriculture are the heavy metals (HMs). Thermal transformation of SS, especially pyrolysis and torrefaction, typically provides pyrolysis oil, pyrolysis gas (syngas), and solid carbonaceous product called either biochar (when used in agriculture) or charcoal. The quality of the biochar depends strongly on the quality of the input dried SS, the amount and types of additives, and the torrefaction conditions. In this work we report the results of the transformation of a mixture of SS from two municipal wastewater treatment plants (WWTPs) with several additives including catalysers (supporting the transformation of SS) and organic additives (increasing the organic carbon content). The aim was to find the optimal conditions for immobilization (i.e. decrease the solubility) of the HMs in SS by thermal transformation. The tests were performed using the full-scale slow microwave torrefaction (MT) unit with 3 kW magnetron with the frequency of 2.45 GHz at low atmospheric pressure. The total HMs content in SS and produced biochars was determined by extraction using *Aqua Regia*, while soluble fraction (bioavailable, potentially harmful fraction) was determined by extraction using deionized water. The analyses revealed significantly low amount of biologically available HMs after MT process in biochars prepared by palletization and with 30% hay (organic additive). Therefore, the slow MT showed its potential to immobilize most of HMs in biochar structure thereby preventing their leaching and decreasing the bioavailability for plants and microorganisms. This is promising for application of biochar in agriculture. It is concluded that MT represents a low energy demanding and easily controllable thermal treatment of SS. The resulting biochar has a great potential to be applied in agriculture.

Table 1 – Feedstock composition from WWTP2, HMs composition in SS and BC – extraction in water

Additive type	Ratio SS:ADD (%)	ID of HMs	Input / output	Extraction in water									
				Cu	Pb	Cd	HMs (mg·kg ⁻¹ DS)			Zn			
				As	Ni	Cr	Hg						
Catalyst	Crushed limestone	C _{SSW}	SS _{IN}	0.560	0.028	0.001	0.156	3.094	0.227	0.018	2.141		
			BC _{OUT}	0.123	0.001	0.001	0.400	0.041	0.006	0.028	0.767		
		C _{BCW}	BC _{OUT}	0.095	0.001	0.001	0.209	0.067	0.003	0.021	0.659		
			BC _{OUT}	0.123	0.001	0.001	0.570	0.095	0.005	0.021	1.036		
		Organic additives	Waste cellulose	C _{SSW}	SS _{IN}	0.503	0.018	0.002	0.106	4.786	0.249	0.025	1.003
					BC _{OUT}	0.154	0.001	0.001	0.305	0.107	0.009	0.018	0.950
C _{BCW}	BC _{OUT}			0.131	0.001	0.001	0.252	0.089	0.006	0.007	0.763		
	BC _{OUT}			0.137	0.001	0.001	0.075	0.087	0.001	0.003	0.392		
Plastic waste (LDPE)	C _{SSW}			SS _{IN}	2.281	0.052	0.001	0.244	2.983	0.140	1.288	0.726	
				BC _{OUT}	0.100	0.020	0.001	0.182	0.038	0.001	0.109	0.015	
Organic additives	Wooden sawdust	C _{SSW}	SS _{IN}	0.092	0.017	0.001	0.475	0.035	0.030	0.124	0.004		
			BC _{OUT}	0.088	0.017	0.001	1.356	0.133	0.006	0.116	0.275		
		C _{SSW}	SS _{IN}	2.243	0.021	0.001	0.154	2.484	0.361	0.025	2.153		
			BC _{OUT}	0.008	0.010	0.001	0.001	5.344	0.008	0.116	0.412		
		C _{BCW}	BC _{OUT}	0.157	0.001	0.001	0.271	0.036	0.009	0.021	0.793		
			BC _{OUT}	0.065	0.001	0.001	0.422	0.022	0.013	0.028	0.640		
Organic additives	Wooden dust	C _{SSW}	SS _{IN}	0.524	0.098	0.001	0.314	2.933	0.170	0.027	1.553		
			BC _{OUT}	0.065	0.001	0.001	0.483	0.025	0.004	0.088	0.492		
		C _{BCW}	BC _{OUT}	0.081	0.001	0.001	0.222	0.044	0.001	0.095	0.355		
			BC _{OUT}	0.092	0.001	0.001	0.612	0.036	0.004	0.088	0.087		
		Hay	C _{SSW}	SS _{IN}	1.072	0.019	0.001	0.106	2.142	0.241	1.072	0.744	
				BC _{OUT}	0.417	0.002	0.001	0.150	0.743	0.201	0.023	1.091	
Organic additives	Husks	C _{SSW}	SS _{IN}	0.006	0.001	0.001	0.001	0.023	0.006	0.133	0.072		
			BC _{OUT}	0.012	0.003	0.001	0.001	0.031	0.012	0.097	0.312		
		C _{SSW}	SS _{IN}	0.278	0.008	0.001	0.078	3.013	0.149	0.026	1.474		
			BC _{OUT}	0.100	0.002	0.001	0.563	0.056	0.102	0.088	0.216		
		C _{BCW}	BC _{OUT}	0.152	0.004	0.001	0.204	0.180	0.008	0.097	0.041		
			BC _{OUT}	0.079	0.001	0.001	0.109	0.025	0.001	0.094	0.290		