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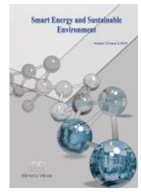

CHARACTERIZATION OF BIOCHAR OBTAINED FROM MANURE AND ENVIRONMENTAL RISK ASSESSMENT

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Abstract:

Animal manure has been used to manage soil fertility since the dawn of agriculture. Applying of this residual organic matter on agricultural soils can cause heavy metals accumulation, migration of pathogens to water sources, and food and generation of greenhouse gases. Biochar obtained through thermochemical conversion shows potential in agronomic uses.
This study investigated the chemical composition and environmental risk of heavy metals in cattle manure and their biochar developed in the thermal range 700°C-850°C.

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1. INTRODUCTION

Since ancient times, people have found various uses for manure. In addition to its main use as a natural soil fertilizer, improving soil fertility and promoting crop growth, manure was, for example, mixed with straw and clay and used in the construction of houses.

These techniques, apparently functional, have certain disadvantages: they cannot cover the entire amount of manure generated, they do not fully exploit the nutritional and economic potential, and most importantly, they do not take into account the environmental repercussions, microbiological and chemical contamination of soil and water with pathogens, heavy metals, antibiotics and other pollutants; greenhouse gases emissions, such as CH_4 and N_2O [J. Meng et al., 2017]. Thus, new, innovative technologies are constantly

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being developed, to transform manure into a raw material for obtaining value-added products while eliminating its negative impact.

Livestock production has increased rapidly in the last century due to increased demand for animal products [L. Bouwman et al., 2011]. In large-scale animal husbandry, trace element additives are widely used as disease prevention agents and growth promoters.

Studies on organic waste have taken a new route, proposing its transformation using thermochemical processes. The advantages of these processes are high productivity, low risk of GHG pollution and the simultaneous obtaining of several valuable products that can be used as raw materials for related sectors, thus focusing on the circular economy.

Pyrolysis has become a universal manure disposal technology, and new approaches present gasification as another rising technology, with even greater thermochemical conversion potential. These processes can modify some characteristics of raw materials and obtain available energy from the gaseous and liquid fractions. Biochar is the carbon-rich product of any biological origin that results from biomass pyrolysis under anoxic conditions at moderate temperatures <700°C [Lehmann J., Joseph S., 2009] or gasification under an oxygen-controlled atmosphere, at higher temperatures (700°C-1000°C). During the pyrolysis of organic waste in biochar, many active functional groups - both electron donors and acceptors - are created. Therefore, the biochar surface shows areas with acidic and alkaline properties demonstrating different affinities to bind water molecules [L. Van Zwieten et al., 2010]. This particular property determines the potential applications of biochar to remove contaminants and reduce the bioavailability of many organic substances (e.g. PHA, PCBs). The pyrolysis and gasification process has the potential to reduce the environmental impact of land application of manure contaminated with heavy metals. The International Biochar Initiative (IBI) developed "The Standardized Product Definition and Product Testing Guidelines for Biochar That Is Used in Soil "(from now on referred to as the "IBI Biochar Standards"), which provides "the tools needed to universally and consistently define what biochar is, and to confirm that a product intended for sale or use as biochar possesses the necessary characteristics for safe use" [International Biochar Initiative, 2015].

The scope of this study included: (1) the production of biochar from cattle manure through pyrolysis and gasification processes under selected temperatures in a hybrid reactor and (2) physicochemical and chemical analysis of cattle manure and thermochemically derived biochar. The presented results contribute to the development of the state of the art, regarding cattle manure biochar adsorption properties under pyrolysis and gasification temperature.

The novelty of this study is represented by the fact that it involved a broader approach, based on both the development of pyrolysis and gasification processes, all of which use a single hybrid reactor, whose construction would allow the retention of the nutrient content in the biochar, transforming it into an effective fertilizer for the degraded soil amendment. The entire paper is focused on the different obtained products, as a function of type of process and process temperature. Through this thermochemical conversion, apart from the biochar, a promising synthesis gas (SG) was developed, with high energy potential through further economical valorization [M. Constantinescu et al., 2024].

2. MATERIALS AND METHODS

2.1. Substrates for Biochar Production

The sample was collected from a farm in Băbeni, Vâlcea, Romania, and during the sampling process, impurities such as leaves, sand and hair were removed manually. Cattle manure, harvested in the spring period of 2023, was naturally dried at room temperature for

48 h to a moisture content (M) <15%, ground to a particle size below 200 µm (*Cutting Mill Pulverisette 15, Germany*), homogenized and stored in a closed container. Sampled cattle manure was analyzed through gravimetric methods to determine M, ash content (A), volatile matters (V) and fixed carbon (FC) in compliance with standardized protocols for solid biofuels, but also through calorimetric methods to determine the calorific value (Qs^{db}) on a IKA 5000, IKA, Germany calorimetric system [M. Constantinescu et al., 2024]. These properties as well as chemical composition are presented in Table 1 and Table 2.

Table 1. The compositional analysis of cattle manure

Proximate (wt%)		**Ultimate** (wt%)	
M^{db}	11.02	N^{db}	2.41
A^{db}	11.02	C^{db}	42.88
V^{db}	67.51	H^{db}	5.60
FC^{db}	10.41	S^{db}	0.40
		O^{db}	26.67
Qs^{db} (kcal/kg)			3604

Note. ^{db} - dry basis

Table 2 Chemical composition of cattle manure ($mg \cdot kg^{-1}$)

Ca	**Mg**	**Na**	**K**	**Cu**	**Mn**	**Zn**	**Pb**	**Ni**	**Cd**
19110.89	3192.26	2718.18	7527.89	235.56	1 14.48	413.22	32.86	21.03	3.24

2.2. Parameters of the Thermochemical Processes

The substrates were subjected to thermal conversion in a fixed-bed, updraft miniHybrid Modular Reactor ($_{mini}$HMR) with a volume of ~ 0.14 L, developed for pyrolysis and gasification experiments, as shown in Figure 1. The $_{mini}$HMR, constructed from stainless steel, was heated with an electric furnace using a PID element. The CO_2 gasification process was carried out at 4 temperatures (700°C, 750°C, 800°C and 850°C) and the pyrolysis process at 750°C. The technical conditions used for the experiments consisted of a gas flow of 100 ml/min, a furnace heating rate of 50°C/min. After achieving the temperature specified for each experiment, a 60-minute residence period was maintained. Once the pyrolysis or gasification process was completed, the heat source was disconnected and the biochar samples were left in the reactor until they reached room temperature, then stored in tightly closed containers at room temperature. The biochar samples produced through the thermochemical conversion of cattle manure are referred to as BCH700, BCH750, BCH800 and BCH850 for CO_2 gasification at selected temperatures, while BCHPM represents the biochar obtained through the pyrolysis process at 750°C.

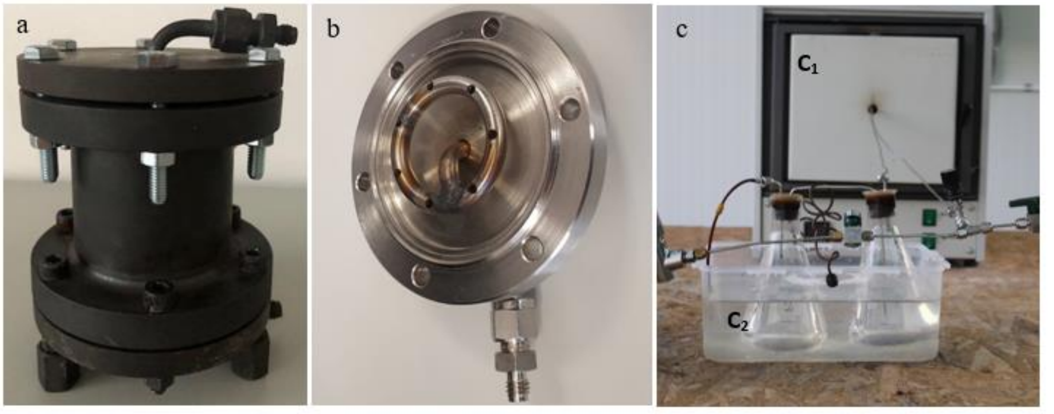

Figure 1. Pyrolysis and gasification hybrid system: a) $_{mini}$HMR; b) lower flange with nozzle system; c_1) electric furnace with PID element, c_2) condensation unit

2.3. Physical and chemical investigations

Cattle manure and the obtained biochar samples were analyzed for moisture content, by oven drying at 105°C, and ash in accordance with ISO standardized method [SR EN ISO 18122, 2023]. The essential organic elements (Carbon, Nitrogen, Sulphur) responsible for greenhouse gases (GHG) formation by combustion, as well as the energy generating ones (Hydrogen, Carbon, Oxygen), were quantified in an innovative way by the combustion/ pyrolysis method coupled with gas chromatography (*EA Flash2000, ThermoScientific, UK*) [ISO 16948, 2015; ASTM D5373, 2021; M. Constantinescu et al., 2019].

The cattle manure and biochar samples were digested in a TOPwave microwave sample preparation system from Analytik Jena equipped with closed Teflon vessels. For the acid digestion procedure, a sample was digested, 0.4±0.05 g, and placed in the digestion vessel with clean Teflon. Then, 6.0 ml of concentrated nitric acid (65%) and 1.0 ml of hydrogen peroxide (30%) were added. The vessel was closed, placed into the rotor, followed by digestion using a three step temperature program, namely (*i*) pressure 40 bar, ramp 5 min, temperature 170°C, time 10 min; (*ii*) pressure 40 bar, ramp 1 min, temperature 200°C, time 15 min; and (*iii*) cooling. The dishes were cooled and opened carefully. After the digestion process, each digested sample was quantitatively transferred with ultra-pure water into a 50 ml volumetric flask.

The leaching tests were conducted according to standardized methods [SR EN 12457-2, 2006]: biochar samples were mixed with distilled water in sealed flasks at a solid-to-liquid ratio (S/L) of 1:10, then shaken on a vertical shaking table over a period of 24 hrs, after which the eluates were filtered using a cellulose filter paper (0.45 µm).

The concentration of elements (Ca, Mg, K, Na, Mn, Zn) was determined by flame atomic absorption spectroscopy method (*NOVAA 300, Analytik Jena, Germany*) and the total concentration of heavy metals (Cd, Ni, Pb, Cu) by graphite furnace atomic absorption spectroscopy method (*GF-AAS Zeenit, Analytik Jena, Germany*).

All chemicals and reagents used during the study were of spectroscopic grade; the ICP Multi-Element Standard Solution XVI Certipur, with a certified value of 100.0 ± 0.3 mg·L^{-1} (*Merck KGaA Frankfurter, Darmstadt, Germany)* was used in the quantitative analysis for the calibration curve. Ultrapure water, having a maximum resistivity of 18.2 MΩ·cm^{-1}, was used for sample treatment and dilution. All the investigated calibration curves were characterized by a high correlation coefficient (r>0.995).

3. RESULTS AND DISCUSSION

3.1. Development of biochar along pyrolysis and gasification processes

The solid residue (biochar) is defined as the non-volatile carbonaceous solid mass resulting from the process of pyrolysis and gasification, collected from inside the miniHMR. It should be noted that the biochar yield along the thermal series is the most constant among all reaction products, ~ 40%, stability due to the release of volatile substances before 700°C, a fact confirmed by the coefficient of variation CV ~ 2% [P. R. Rout et al., 2023], Figure 2.

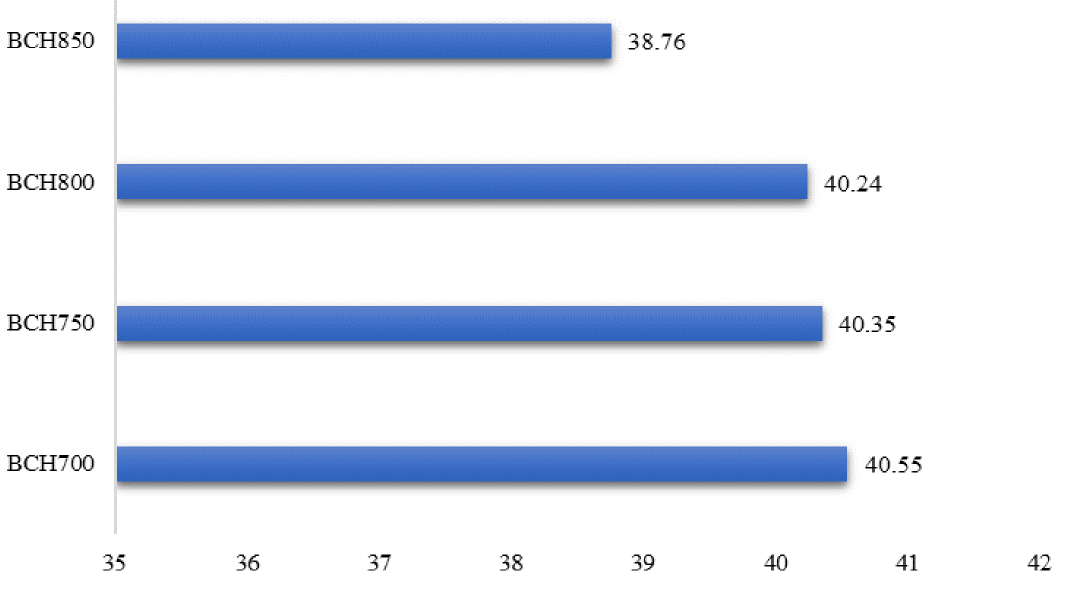

Figure 2. Biochar yield (%) along the thermal series, BCH700; BCH750; BCH800; BCH850

On the other hand, the biochar yield decreasing along the temperature elevation range, can be explained by the increase in the energy of the C atoms, determining the C-C bonds of the aromatic ring to easily break and generate more molecules of $_{active}C$. The effective collision time between the $_{active}C$ molecules and the process agent was increased, explaining the accelerated reaction speed [M. Ma, et al., 2020]. The average yield obtained is in the upper third of the field offered by the specialized literature, 24.49% - 42.5%, [S-S. Kim et al., 2019; M. Azuara et al., 2013; A.E. Erdogdu et al., 2019]. The high process temperatures left behind a structure composed mostly of a C skeleton, indicating that the degree of order of the C microcrystalline structure of the solid residue sample actually increases. This is due to the fact that the organic matter released structures such as O-containing functional groups, aliphatic chains and bonds common to aromatic clusters that gradually yield with increasing process temperature. Then, the dehydrocondensation of the structure of the rest of the aromatic rings takes place, and the size of the aromatic C skeleton gradually increases until it approaches the structure of graphite [C. Li, 2004]. The temperature variable had a major influence on the yield along the tested thermal series, namely at 800°C the most homogeneous series of values developed, CV ~0.81%, and at 850°C the lowest concentration.

Table 3. Compositional evolution under the influence of temperature (wt%)

Parameter type	*Sample type*					
	cattle manure	BCH700	BCH750	BCH800	BCH850	BCHPM
N^{db}	2.41	1.44	1.33	1.24	0.92	1.97
C^{db}	42.88	32.34	33.32	35.96	36.03	34.51
H^{db}	5.60	0.91	0.86	0.82	0.58	1.54
S^{db}	0.40	0.26	0.24	0.25	0.18	0.17
M^{db}	11.02	0.54	0.22	0.15	0.09	0.62
A^{db}	11.02	55.23	55.89	56.17	57.53	55.72
$^*O^{db}$	26.67	9.28	8.14	5.41	4.67	5.47

**Note. The oxygen concentration was determined by the difference. ^{db} - dry basis*

Table 3 characterizes the biochar obtained through gasification and pyrolysis processes, over the temperature range used for each experiment. Although decreasing in relation to the value from the cattle manure of ~43wt%, the slight increase in the concentration of C in the case of gasification processes with the increase in temperature is motivated by the release of volatile matters. The yield of solid residue is directly related to the high content of metals in the feedstock which led to a higher yield of C [F.A. Agblevor et al., 2010].

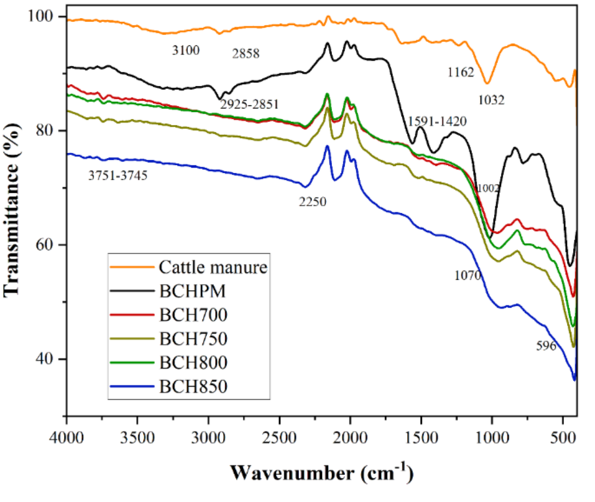

Figure 3. FT-IR spectra of cattle manure and solid residue resulting from the pyrolysis and gasification processes

The concentrations (wt%) of N, H and O in the biochar decreased with the increase of the process temperature, in opposition with C behaviour. The decrease in O content is caused by the dominant reactions of dehydration and decarboxylation at higher temperature. As the temperature increases, the cattle manure is subjected to thermochemical destruction to produce a high-quality carbonaceous solid, and according to the Van-Krevelen diagram, it is in the region of lignite-type coal [R. Azargohar et al., 2016]. The chemical functional groups present on the biochar surface were examined using the FT-IR method (*Agilent Cary630, USA*). Figure 3 shows the spectra of cattle manure and the resulting biochar, respectively the distribution of functional groups, depending on the type and the process variables run. In the case of cattle manure, FT-IR revealed the complexity of functional groups present in the content of minerals and organic matter [W-T. Tsai, S-C. Liu, 2016]. The peak that appears at 3100 cm^{-1} represents –H linked to the –OH group, potentially caused by the release of a low amount of intramolecular moisture. The vibration located at 2858 cm^{-1} was attributed to the presence of aliphatic C–H. All the peaks and bands that appear between 1700-1300 cm^{-1} were produced by the bending absorbance specific to alkanes, correlated with the characteristic stretches of the alkene C=C, the nitro N–O group, the aromatic ring band and the carbonyl C=O groups as a carboxylic bond. The sharp peak at 1032 cm^{-1} is associated with aromatic ethers and C–H polysaccharides, and the segment 1162-1000 cm^{-1}, with mineral components associated with phosphate (PO_4^{3-}) and carbonate (CO_3^{2-}). The biochar specific spectra were almost similar for the gasification processes, at the 4 selected temperatures. The low-intensity peaks from 3751-3745 cm^{-1} were attributed to -OH and -NH stretching vibrations originating from various organic compounds [X. Cao, W. Harris, 2010; S. Mia et al., 2017]. A peak of reduced intensity can be seen at 2250 cm^{-1} attributed to the symmetric stretching vibration of the aliphatic C-H bond in the polymers [K.B. Cantrell et al., 2012]. The P-O bond in organic and inorganic phosphates (PO_4^{3-}) can be identified at 1070 cm^{-1}. This peak is also the result of multiple overlapping bands, also correlated with C-O bond stretching present in cellulose, hemicellulose and lignin found in cattle manure [R.K. Sharma et al., 2004]. However, among all the processes, the BCH850 stands out, in which case the baseline is more inclined due to infrared light scattering, and the peak at 596 cm^{-1} can be attributed to the Fe-O vibration [R.W. Jones et al., 2012; M.M. Mian et al., 2018].

Major differences were identified in the case of the char resulting from the pyrolysis process, among which the appearance of a double peak at 2925-27851 cm^{-1} attributed to the asymmetric stretching vibration of the aliphatic C-H bond in polymers [U.S. Environmental Protection Agency. Operating Anaerobic Digester Projects, 2014; L. Zhao et al., 2013], the C=C stretching peaks and C=O from 1561-1420 cm^{-1} due to aromatics [U.S. Environmental Protection Agency. Operating Anaerobic Digester Projects, 2014], and an intensification of the peak at 1025 cm^{-1} attributed to P-O bonds from organic and inorganic phosphates (PO_4^{3-}) [W-T. Tsai, S-C. Liu, 2016; U.S. Environmental Protection Agency. Operating Anaerobic Digester Projects, 2014; L. Zhao et al., 2013].

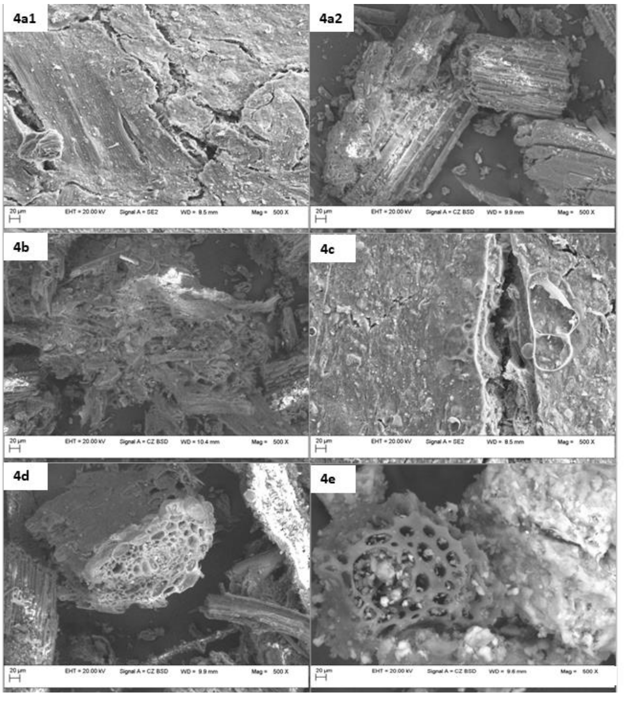

Figure 4. SEM micrographs of cattle manure and derived biochar, a_1/ a_2 - cattle manure; b - BCH700; c - BCH750; d - BCH800; e - BCH850

Table 4. BET/BJH morphostructural investigations

Sample type	*Parameter type*		
	S_{BET}, m^2/g	V_p, cm^3/g	Dv (r), *Å*
Cattle manure	0.955	0.004	15.653
BCH700	1.612	0.006	18.881
BCH750	1.759	0.011	18.907
BCH800	1.782	0.013	19.669
BCH850	2.372	0.021	21.675

The morphostructural surface characteristics evolution is presented in Figure 4 and Table 4. In the case of dry cattle manure, SEM (*Carl Zeiss, USA*) micrographs indicate irregular and agglomerated structures, with a rough texture, without well-defined pores, with abundant parallel lines, which serve as transport pathways for soil nutrients and water, Figure 4a. The vascular structure, with cell walls and open vessels, is specific to herbaceous plants with a lignocellulosic constitution. For BCH700 and BCH750, respectively after the thermochemical processes, the morphology is not completely different, with a rocky, flat structure, with the presence of unburnt ash residues, suggesting an incomplete conversion of the processes, Figure4 b,e [M. A. Shah et al., 2023]. Micrographs identify large, irregular particles and granules with high cellulose content, which are due to increased restrictions on molecular motion during thermochemical processes at high temperatures. However, it can be seen that the BCH700, Figure 4b, possesses more cavernous structures and/ or cracks than the more compact BCH750, Figure 4c, with fewer pore structures and a higher C content, Table 4. The darker region represents the crystalline C structure of the solid residue formed, and the whiter region around the caverns represents the ash supported by it. Cattle manure typically has a high organic content and cellulosic composition due to bacterial and chemical reactivity along the animal's digestive tract. The solid samples were investigated by BET (*Autosorb-iQ-C, USA*), monitoring possible surface changes throughout the sequence of chemical, thermal and physical transformations.

The data showed that, under the action of temperature, the specific surface area of the solid residue changed significantly, that is, the average pore volume increased from ~15 Å to ~21 Å naturally by unblocking the coke pores. The phenomenon is doubly validated, (i) by increasing the total pore volume from ~ 0.004 cm^3/g to 0.021 cm^3/g, respectively by (ii) chancing the BET surface area from 0.9 m^2/g to 2.3 m^2/g. The specific surface, with a crucial role in the adsorption of organic compounds and/ or CO_2, higher in the case of activated BCH850, was favored by the efficiency of penetration of cellulose, lignin, hemicellulose by the inert N_2 atmosphere, but also by the level of high temperature [M. Inyang et al., 2012]. Chemical phenomena are complemented by physical ones, during pyrolysis producing high fluidity and gases due to the release of a large amount of volatile matter, traveling through the fluid mass and developing a vacuolated heterogeneous structure [A.A. Yusuf et al., 2020].

3.2. Chemical Composition of Biochar

The produced biochar samples were subjected to chemical analysis and are present in Table 5. The content of Ca in biochar was in the range of 12646.26–15444.57 mg·kg^{-1} the higher values being associated with elevated temperatures. The same trend is observed for Mg which was in the range of 5505.18–7052.97 mg·kg^{-1} in the produced biochar. The presence of Ca and Mg could have a predominant effect on the adsorption of other ions by biochar [L. Zhang et al., 2019].

Potassium content is significantly higher than sodium. Potassium is an inorganic mineral element in biomass and has a significant catalytic effect on biomass thermochemical conversion. Due to its low thermostability, organic potassium is released from biomass and converted to the gas phase at low temperatures (500°C); at high temperatures, inorganic potassium in biomass enters the gas phase due to increased vapor pressure in the biomass. The regulation and control of process temperature have a significant effect on the structure and amount of potassium in the biochar.

The produced biochar samples were also tested for the concentration of the following heavy metals: Cd, Pb, Cu, Ni, Zn and Mn the results presented in Table 5. Heavy metals can exist in various chemical forms in manure, such as hydroxides, oxides, and sulphides. In particular, hydroxides and mineral salts tend to be converted into compounds with better thermal stability. When exposed to high temperatures, these forms of heavy metals do not decompose or chemically change as easily as other forms, such as sulphides. These compounds become more resistant to high temperatures and may not volatilize or decompose easily during thermal processes. Cd, Zn and Pb can easily form more volatile chemical compounds ($CdCl_2$, $ZnCl_2$ and $PbCl_2$). The distribution patterns of heavy metals followed the decreasing trends of Cu>Mn>Zn>Pb>Ni>Cd.

For all the biochar samples analyzed, the concentrations of Cd and Zn decreased compared to the concentrations in the raw material (Table 2), as in the temperature range of 700°C-850°C, these elements underwent an evaporation process due to their low boiling points. In the case of Zn, this evaporation mechanism is positively correlated with the increase in process temperature. CO_2 gasification has no major impact on metal retention when compared to other atmospheres like air or nitrogen, as Cantrell et al. (2012) [K.B. Cantrell et al., 2012] observed a similar temperature trend concentration in biochar samples produced from a variety of manure feedstock at pyrolysis temperatures between 350°C and 700°C. Heavy metals such as Cu, Pb and Ni did not show a clear trend of increasing or decreasing concentration as a function of temperature.

Table 5. Chemical composition of cattle manure derived biochar samples (mg·kg^{-1} dry wt)

Biochar type	***BCH700***	***BCH750***	***BCH800***	***BCH850***	***BCHPM***	***Toxicant assessment (IBI)***
Ca	13718.92	15444.57	15212.43	15072.74	12646.26	-
Mg	7052.97	6945.12	7050.02	6847.45	5505.18	-
Na	2547.03	2479.69	2755.82	2846.60	3085.06	declaration
K	24075.68	23347.97	22864.32	21566.11	22727.27	-
Cu	428.22	422.61	433.07	468.66	502.36	143-6000
Mn	274.59	276.40	293.74	238.23	282.07	-
Zn	166.59	131.72	72.86	49.04	184.29	416-7400
Pb	76.58	80.57	75.80	79.91	86.30	121-300
Ni	33.30	37.95	39.62	40.98	50.41	47-420
Cd	1.83	2.00	1.00	1.13	1.21	1.4-39

The International Biochar Initiative had provided quality guidelines for permissible limits of 13 toxic elements (TEs) to be applied to the soils. Comparisons with the permissible IBI limits indicated that none of the biochar samples exceed the TE accepted content, Table 5.

3.3. The leaching test

One method for evaluating hazardous substances released from waste is the leaching test. The method used is that described in accordance with ISO standardized method [SR EN 12457-2, 2006]. Test results indicate water-soluble inorganic contaminants that are available to plants and easily transported through the soil.

In Table 6 are evidenced the heavy metal values in aqueous biochar extracts. The concentrations of metals obtained were compared with the limit values and with the waste acceptance values for landfilling [Order No 95 of 12 February 2005], and it was found that their level is negligible.

Table 6. Concentration of metals ($mg \cdot kg^{-1}$) in aqueous extracts of biochar (1:10)

Sample type	**Cu**	**Zn**	**Pb**	**Ni**	**Cd**
BCHPM	0.32	<1.00	0.09	0.04	0.004
BCH850	0.16	<1.00	0.22	<0.02	0.004
Regulated maximum levels admitted [0]	2.00	4.00	0.50	0.40	0.04

3.4. Geochemical quality assessment of biochar

In this study, the contamination factor (C_f) and the contamination degree (C_d) were selected to guide the individual and the total elemental enrichment, respectively. These indices were described by Qingjie et al., 2008 [G. Qingjie, 2008], Hakanson, 1980 [L. Hakanson, 1980] as being successful in assessing the quality of environmental matrices.

3.4.1. Contamination factor

The contamination factor was calculated according to the formula:

$$C_f^i = \frac{C_i}{C_{ri}} \quad (1)$$

where C_i is the concentration of metal *i* (in the cattle manure, respectively in BCH) and C_{ri} is the concentration of the metal *i* (background value, respectively in the cattle manure).

Table 7. Contamination factor (C_f) of toxic elements in cattle manure

	C_f^{Cu}	C_f^{Mn}	C_f^{Zn}	C_f^{Pb}	C_f^{Ni}	C_f^{Cd}
cattle manure	23.6	0.5	10.3	1.6	1.1	32.4
Contamination state	very high	low	very high	moderate	moderate	very high

Table 8. Contamination factor (C_f) of toxic elements in biochar

Biochar type	C_f^{Cu}	C_f^{Mn}	C_f^{Zn}	C_f^{Pb}	C_f^{Ni}	C_f^{Cd}
BCH700	1.8	2.4	0.4	2.3	1.6	0.6
BCH750	1.8	2.4	0.3	2.5	1.8	0.6
BCH800	1.8	2.6	0.2	2.3	1.9	0.3
BCH850	2.0	2.1	0.1	2.4	1.9	0.3
BCHPM	2.1	2.5	0.4	2.6	2.4	0.4
Contamination state	moderate	moderate	low	moderate	moderate	low

The following terminologies are used to describe the contamination factor: $C_f^i < 1$, low contamination factor; $1 \leq C_f^i < 3$, moderate contamination factors; $3 \leq C_f^i < 6$, considerable contamination factors; and $C_f^i \geq 6$, very high contamination factor.

The results (Table 8) show that the environmental risk of heavy metals in biochar has decreased compared to that in manure as the process temperature increased from 700°C to 850°C.

3.4.2. Contamination degree

The contamination degree was calculated according to the formula given by Hakanson (1980) [L. Hakanson, 1980] and it is equal to the sum of all the contamination factors:

$$C_d = \Sigma_{i=1}^{n} C_f^i \qquad (2)$$

Table 9. Contamination degree (C_d) of toxic elements in the cattle manure and derived biochar

Sample	Contamination grade	Value grade standards	Contamination state
Cattle manure	69.5	$C_d<8$	Moderate degree of contamination
BCH700	9.1	$8 \leq C_d < 16$	Moderate degree of contamination
BCH750	9.4		
BCH800	9.1	$16 \leq C_d < 32$	Considerable degree of contamination
BCH850	8.9		
BCHPM	10.4	$C_d>32$	Very high degree of contamination

Compared to the value grade standards presented in Table 9, all biochar samples exhibit a moderate level of contamination. The results suggest that pyrolysis and gasification are beneficial in reducing the risk of environmental contamination with heavy metals.

4. CONCLUSIONS

Concentration levels of toxic and non-toxic elements in tested biochar vary with temperature. However, concentrations of toxic elements do not exceed the permissible IBI limits for land application.

Leaching tests showed negligible leaching of heavy metals from the biochar samples tested.

Analysis of biochar samples in terms of contamination factor (C_f) showed a low risk of contamination for cadmium and zinc and a moderate risk for copper, manganese, lead and nickel.

The results developed in the present research show that biochar production using wastes with high levels of heavy metals should be properly handled. There is a need for continuous monitoring of biochar before and after its introduction into soils amendment.

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