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Characterization of Steam Gasification Biochars from Lignocellulosic Agrowaste Towards Soil Applications

Lina María Romero Millán[1,2] · Fabio Emiro Sierra Vargas[1] · Ange Nzihou[2]

Abstract

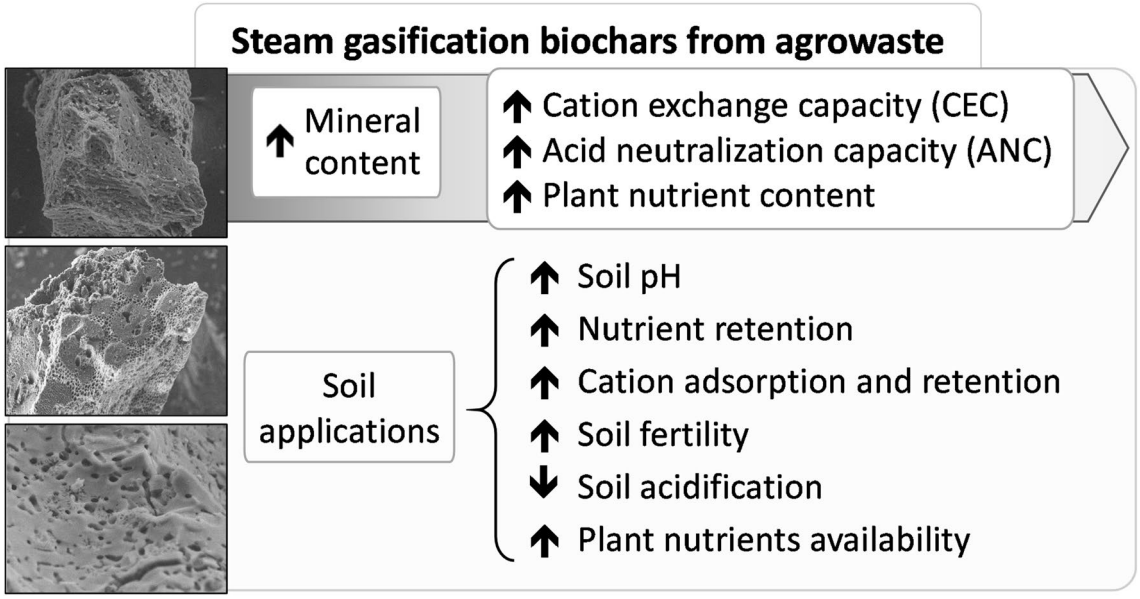
The main objective of this work was to analyze the physico-chemicals properties of biochars produced from the steam gasification of different lignocellulosic agrowastes, and determine the suitability of these materials to be used in soil amendment and remediation applications. Steam gasification biochars from three lignocellulosic agrowastes were extensively characterized. Coconut shells (CS), bamboo guadua (BG), and oil palm shells (OPS) were chosen as raw materials, considering their different macromolecular structure and inorganic composition. The biochars composition, morphology, pH, acid neutralization (ANC) and cation exchange (CEC) capacities, as well as their mineral release at different conditions were evaluated and compared. The experimental results showed that the inorganic content and composition of the biochars have a stronger impact on their properties for soil applications, in comparison to their organic composition and morphology. In particular, BG biochar, the sample with the highest mineral content, exhibited the most notable cation exchange (45 $cmol_c/kg$) and acid neutralization capacities (125 cmol H^+/kg), together with the greatest release of plant micro and macro-nutrients. In the case of biochars with low mineral content, higher CEC and ANC were most related to the presence of oxygen-containing functional groups in their surface. Considering that agricultural residues come from numerous sources and activities, the presented results usefully contribute to the comprehension of the relationship between the raw biomass characteristics, the physico-chemical properties of steam gasification biochars, and their expected performance in soil applications, opening a new promising valorization pathway for these materials.

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Graphic Abstract



Keywords Lignocellulosic biomass · Agrowaste valorization · Steam gasification biochar · Mineral release · Soil amendment and remediation

Statement of Novelty

In this work, the extensive characterization of steam gasification biochars from three different agrowastes was performed, presenting a valorization alternative for these materials in soils. Usually, pyrolysis biochars are used in soil applications thanks to their physico-chemical properties, while gasification biochars are rarely considered. Yet, the latter ones may also have interesting characteristics in this field that should be evaluated. In addition to the composition and morphology characterization, common in literature, the assessment of other properties like pH, pH_{PZC}, cation exchange (CEC) and acid neutralization capacities (ANC), and mineral content and release was also performed. Accordingly, this work contributes to the comprehension of the relationship between the biomass characteristics, the properties of gasification biochars, and their expected performance in soil applications.

Introduction

Agroindustrial activities all around the world produce great amounts of low-cost residues that could be used for biofuel production or transformed in value-added products. However, in most cases, agrowastes are barely valorized and remain underexploited. In this context, steam gasification could be an interesting process for the simultaneous production of high heating value fuel gases for heat or power generation, and a porous carbon-based by-product, also called biochar, that could be valorized [1–3].

Biochars are carbon-rich porous materials with versatile physico-chemical properties. They exhibit a high carbon content, large porosity and specific surface area, high adsorption capacity, and great thermal stability [4]. In accordance, they can be valorized in diverse applications, including heat and power generation, catalysis, pollutant uptake, carbon sequestration, and soil amendment or remediation [5, 6]. Considering the importance of agroindustrial activities for the economy of several developed and developing countries, the use of gasification-based biochars in soil applications might be considered as an effective approach to enhance soil fertility and improve crop yield, developing a circular economy strategy [7].

Regarding soil amendment and remediation, pyrolysis-based biochars usually show a high cation exchange capacity (CEC), associated with an important ability to adsorb and retain cations, improving nutrient retention and availability in soils [8]. This capacity may also contribute to the removal and immobilization of heavy metals, making them unavailable for leaching or plant uptake [9]. Moreover, the high alkalinity of biochars suggests the use of these materials for the improvement of acidic soils properties. In relation

to this, several authors have found that pyrolysis-based biochars may improve the physical properties of different kinds of soils, increase their cation exchange (CEC) and acid neutralization capacities (ANC), and enhance the availability of nutrients for plant uptake, promoting their retention and avoiding their leaching [10–12].

Nevertheless, the impact of biochars in soils largely depends on their physico-chemical properties, generally determined by the raw material and the production conditions [13–16]. For instance, in the case of pyrolysis-based biochars, widely studied and used for soil applications, higher CEC has been observed for low-temperature treatments, considering the low volatilization extent attained. In consequence, low-temperature biochars usually show a better performance in soil applications, in comparison to high-temperature samples [17, 18].

Contrary to pyrolysis biochars, the use of gasification solid by-product is not often reported in the literature, considering that the gasification process is usually focused on gas production. However, as gasification-based biochars are generally produced at higher temperatures and under a reactive atmosphere, their physico-chemical properties may vary from those of pyrolysis, and should be carefully analyzed to determine their suitability in soil applications [19]. In particular, when steam is used as gasifying agent, the associated solid by-product may develop larger porosities and specific surface areas in comparison to pyrolysis biochars, and may have an important amount of oxygen-containing functional groups that could enhance properties like cation exchange (CEC) and acid neutralization capacities (ANC) [20–22]. These properties, particularly interesting for soil amendment applications, may open a valorization pathway for gasification biochars. In relation to this, a higher soil amendment and remediation effectiveness has been observed for different activated carbons in comparison to pyrolysis biochars [23–26], suggesting that the steam gasification process could also produce solid by-products with interesting properties in this field. Moreover, due to the high mineral content of agrowastes, gasification biochars from these feedstocks could be also a direct source of plant macro and micronutrients (e.g. N, P, S, Ca, Mg, Zn, Mn, Cu, B, Mo, Co, Fe, and Ni), and other beneficial elements (e.g. Na, Co, Si, Se, and V), promoting soil fertility and plant growth [27, 28].

Considering that agricultural residues come from numerous sources and activities, the associated steam gasification biochars may have variable physicochemical properties, depending on the composition and structure of the raw material. In consequence, their performance in soil applications may differ. In this regard, the influence of the raw biomass characteristics on the properties of steam gasification biochars needs also to be evaluated. In particular, the physico-chemical characterization of biochars is usually focused on their organic composition, morphology, and porous structure. However, the assessment of other properties like pH, pH_{PZC}, cation exchange capacity (CEC), acid neutralization capacity (ANC), mineral content, and mineral leaching behavior may also be of great interest to properly determine the suitability of these materials in the proposed environmental application.

In this regard, an extensive analysis of the physico-chemical properties of steam gasification biochars produced from lignocellulosic agrowastes was performed in this work. Thus, coconut shells (CS), bamboo guadua (BG) and oil palm shells (OPS) were strategically selected as raw materials, considering their different macromolecular structure and inorganic composition. This choice might give an interesting outlook to the properties of steam gasification biochars from a wide range of lignocellulosic feedstocks. The evaluation and comparison of the biochars morphology, pH, buffering capacity, CEC, and mineral release at different conditions, revealed the potential of these materials in environmental applications, to enhance soil fertility and agricultural productivity. Accordingly, the agronomical implications of the observed gasification biochar properties were discussed, providing new insights to the selection of potential feedstocks and process conditions, for the preparation of biochars intended for environmental applications.

Materials and Methods

Raw Materials

Steam gasification biochars obtained from three tropical lignocellulosic agrowastes were characterized and analyzed in this study. Coconut shells (CS), bamboo guadua (BG), and oil palm shells (OPS) were selected as raw materials, considering their different macromolecular and inorganic composition, determined according to the standards of solid biofuels (detailed in previous works [29, 30]), and summarized in Table 1.

Gasification Experiments

Biomass gasification experiments were performed in a semi-continuous laboratory-scale fluidized bed gasifier, described in detail in a previous work [3]. For all the experiments, 80 g of biomass with particle size between 1 mm and 3 mm were placed inside the reactor and heated to 850 °C, under nitrogen, with a heating rate of 20 °C/min. When the temperature was reached, the atmosphere was switched to a mixture of 30% steam/70% N_2 (vol.%), with a total flow rate of 0.7 m^3/h. The steam mass flow rate supplied to the process was 100 g/h. Gasification experiments were stopped after 1 h, to maximize the quantity of recovered char for further analysis. The reactor was then cooled down to room

Table 1 Organic and inorganic composition of the raw biomass and the analyzed biochars

Raw biomass				
		CS	BG	OPS
Elemental analysis (wt% dry basis)	Organic composition			
	C	46.8 ± 0.2	42.7 ± 0.3	46.7 ± 0.2
	H	5.8 ± 0.1	5.4 ± 0.1	6.5±0.1
	O[a]	47.1 ± 0.1	51.5 ± 0.1	46.2 ± 0.1
	N	0.3 ± 0.1	0.4 ± 0.1	0.6 ± 0.1
	Ash	1.4 ± 0.1	5.0 ± 0.4	1.7 ± 0.2
Essential plant nutrients (mg/kg dry basis)	Primary macronutrients			
	P	396.7 ± 4	828.6 ± 6	270.0 ± 7
	K	2 807.8 ± 4	5 360.1 ± 8	1 006.5 ± 15
	Secondary macronutrients			
	Ca	391.4 ± 7	441.3 ± 9	53.8 ± 6
	Mg	170.4 ± 15	172.7 ± 1	135.2 ± 3
	Micronutrients			
	Mo	10.82 ± 6	n.d.[b]	n.d.[b]
	Zn	32.8 ± 12	2.0 ± 1	0.5 ± 2
	Mn	45.4 ± 16	18.8 ± 13	35 ± 17
	Cu	173.8 ± 31	98.4 ± 17	138 ± 25
	Ni	108.2 ± 25	n.d.[b]	144.2 ± 22
	Fe	159.8 ± 2	116.0 ± 1	107.4 ± 4
	Beneficial nutrients			
	Na	330 ± 1	200 ± 0.8	15 ± 0.5
	Si	309.3 ± 4	19 372.1 ± 354	5 600.0 ± 3
Macromolecular composition (wt% daf)[c]	Cellulose	32.5	53.9	30.4
	Hemicellulose	20.5	13.5	12.7
	Lignin	36.5	25.1	49.8
Steam gasification biochars				
		CS biochar	BG biochar	OPS biochar
Elemental analysis (wt% dry basis)	Organic composition			
	C	79.2 ± 1.3	60.8 ± 1.5	85.2 ± 2.1
	H	1.3 ± 0.2	0.8 ± 0.1	0.8 ± 0.1
	N	0.1 ± 0.1	0.3 ± 0.1	0.5 ± 0.1
	O[a]	11.3 ± 1.2	6.6 ± 1.3	8.6 ± 2.0
	Ash	8.2 ± 1.1	31.5 ± 1.2	4.9 ± 0.9
	O/C	0.11	0.08	0.08
	H/C	0.22	0.17	0.11
	VM[d]	16.2 ± 0.5	10.5 ± 0.3	9.7 ± 0.5

Table 1 (continued)

Steam gasification biochars				
		CS biochar	BG biochar	OPS biochar
Essential plant nutrients (mg/kg dry basis)	Primary macronutrients			
	P	274.0 ± 59	1 930.9 ± 840	2 255.7 ± 97
	K	20 393.8 ± 2 520	30 501.9 ± 367	6 375.3 ± 958
	Secondary macronutrients			
	Ca	387.7 ± 185	1 264.3 ± 206	1 560.9 ± 49
	Mg	320.1 ± 121	785.9 ± 127	1 623.2 ± 103
	Micronutrients			
	Mo	17.1 ± 15	16.6 ± 23	41.4 ± 50
	Zn	162.9 ± 30	179.0 ± 55	n.d.[b]
	Mn	170.3 ± 48	184.5 ± 105	129.0 ± 80
	Cu	561.2 ± 14	632.5 ± 324	276.1 ± 14
	Ni	189.1 ± 54	35.9 ± 25	444.8 ± 110
	Fe	1 270.0 ± 150	1 332.8 ± 840	888.6 ± 105
	Beneficial nutrients			
	Na	4 188.7 ± 823	376.5 ± 58	101.2 ± 24
	Si	954.6 ± 38	86 598.5 ± 20 516	13 477.1 ± 3 925
pH and pH_{PZC} (−)	pH (H_2O)	10.2 ± 0.1	10.9 ± 0.1	9.8 ± 0.3
	pH_{PZC}	2.2 ± 0.3	1.6 ± 0.3	3.1 ± 0.2

[a]Calculated by difference: O (wt% dry basis) = 100-C-H-N-S-Ash

[b]Not detected

[c]From [30]

[d]Volatile matter (wt% dry basis)

temperature under an inert atmosphere, and the remaining biochar was collected. The biochar yield (wt.%) at the end of the gasification process was around 12%, 13%, and 23% for CS, BG, and OPS respectively.

Char Characterization

Elemental Composition and Ash Content

The organic composition (CHNS) of the studied biochars was established using a Thermo-quest NA 2000 elemental analyzer, according to the standard EN ISO 16948. The oxygen content was obtained by difference. The ash content of the samples was calculated according to the standard EN ISO 18122. The mineral composition was determined using an HORIBA Jobin Yvol Ultima 2 inductively coupled plasma optical emission spectrometer (ICP-OES), according to the experimental procedure described in the standard EN 16967. All the analyses were performed with at least three replicates. The local chemical composition of the samples at a micro-scale was also analyzed using a Hitachi TM3030 Plus tabletop scanning electron microscope (SEM), with an energy-dispersive X-Ray spectroscopy (EDX) module in the same apparatus.

pH and pH_{PZC}

The pH of biochars in aqueous solution was measured following the experimental protocol proposed by Denyes et al. [31], by adding 0.25 g of sample to 25 ml of distilled water. The suspension was shaken for two minutes and then centrifuged to collect the supernatant. The pH was measured using a calibrated Hach PHC725 probe. The pH at the point of zero- charge (pH_{PZC}) of each sample was measured using a Malvern Pananalytical Zetasizer NanoZS. 15 mg of biochar (ground into powder, with a particle size below 250 µm) were used for each test with a sample concentration of 0.5 mg/ml. Then, electrical charge density measurements were performed at room temperature, within the pH range from 2 to 11, adjusted by the addition of a 0.25M hydrogen chloride (HCl) or 0.1M

sodium hydroxide (NaOH) solution. The biochar pH_{PZC} was defined as the pH at which the electrical charge density measured on the surface was zero [32].

Cation Exchange Capacity (CEC)

The cation exchange capacity (CEC) of biochars was measured according to the sodium acetate method described by Laird and Fleming [33]. 0.2 g of raw biochar (not ground) were placed in a 50 ml centrifuge tube and washed three times with a 1M sodium acetate (NaOAc) solution with a pH adjusted to 8.2. The samples were then rinsed with a 80% isopropanol solution followed by pure isopropanol until the measured electrical conductivity of the supernatant solution was below 1 µS/cm. Finally, the retained Na^+ was displaced washing the sample three times with a 0.1M ammonium chloride (NH_4Cl) replacing solution. The extracted sodium content was analyzed using inductively coupled plasma-atomic emission spectrometry (ICP-OES), and the CEC of the samples in cmol/kg was calculated according to Eq. 1.

$$CEC = \frac{100 \cdot C \cdot V}{W \cdot m_m} \quad (1)$$

Where C is the measured, Na concentration in mg/L, V is the dilution volume of the analyzed solution in L, W is the sample mass in g, and m_m is the sodium molar mass in g/mol.

Acid Neutralization Capacity (ANC) and Mineral Release

The biochar acid neutralization capacity (ANC) and the leaching behavior of inorganic constituents were determined using the protocol described in the NF EN 14429 standard. Samples were leached with water solutions containing pre-selected amounts of acid or base, to reach specific pH values at the end of a 48 h extraction period, within the pH range from 2 to 12. Preliminary titration tests were performed to determine the acid and base quantities required to obtain at least 8 final pH values within the analyzed range. 5M nitric acid ($HNO_{3)}$ and 2.5M sodium hydroxide (NaOH) solutions were used to adjust the solution pH. For each test, 750 mg of raw biochar (not ground, 2–4 mm particle size) were leached using a liquid to solid ratio of 10 L/kg. The suspensions were mixed using a GLF 3040 rotating shaker at 6 rpm during 48 h. At the end of the test, the pH of the suspensions was measured using a Hach PHC725 probe. The liquid phase was separated from the solid by filtration, and analyzed using inductively coupled plasma-atomic emission spectrometry (ICP-OES).

Surface Oxygen-Containing Functional Groups (SOFG)

The oxygen-containing functional groups in the biochar surface were determined using temperature-programmed desorption (TPD) analysis. Experiments were performed using a Micromeritics AutoChem II chemisorption analyzer. 150 mg of biochar (ground into powder, with a particle size below 250 µm) were placed in a quartz U-tube and heated under a helium atmosphere. The sample was kept at 150 °C during 1 h and then was heated to 1000 °C with a heating rate of 5 °C/min. The concentration of CO and CO_2 released was quantitatively analyzed using a MyGC Agilent micro-GC. The repeatability of the TPD tests was found to be satisfactory with a maximum calculated standard deviation below 10% for at least three replicates. To determine the contribution of each type of oxygen complex, both the CO and CO_2 desorption curves were deconvoluted using six Gaussian peaks according to the procedure proposed by Zhou et al. [34], and detailed in a previous work [3]. The fitting error found between the experimental and the deconvoluted curve was always below 8%.

Pore Volume and Specific Surface Area

The specific surface area and pore volume of biochars were determined by nitrogen adsorption at 77 K using a Micromeritics 3Flex high-resolution analyzer. Prior to measurements, the samples were degassed in vacuum at 90 °C for 1 h and then at 150 °C for 10 h. The surface area was calculated from the adsorption isotherms using the Brunauer–Emmett–Teller (BET) model. The t-plot model was used to determine the micropore volume of samples. The repeatability of the tests was also found to be satisfactory.

Results and Discussion

Composition of Gasification Biochars

Table 1 reports the organic and inorganic composition of the selected feedstocks and their associated steam gasification biochars. It can be observed that the three analyzed biochars are highly carbonaceous materials with carbon content between 60% and 85%. BG biochar exhibited the lowest carbon percentage, considering its high ash content (above 30%), in comparison to CS and OPS biochars (below 10%). It is worth noting that the mineral constituents and distribution of the biochars were directly related to the composition of the raw biomass. In particular, CS biochar was mainly composed of K, Ca and Na, while the main constituents of

BG and OPS biochars were Si, P, and K. The presence of heavy metals like Hg, Pb, Cd, or As was not detected, either in the raw biomass or the resulting biochars.

In general, the mineral concentration in biochars was significantly higher in comparison to the raw materials, as a result of the solid conversion taking place during the gasification process. The observed mineral retention level in the biochars with respect to the raw materials was between 70% and 80%, considering an average biochar yield of 13%, 16% and 21% for CS, BG, and OPS respectively (under the analyzed gasification conditions). In fact, a certain amount of minerals may volatilize during the gasification process, depending on the temperature and solid conversion level [35–37]. In particular, K showed low volatilization levels (< 10%), while Ca and Mg exhibited higher volatilization degrees (> 30%). Si and P also showed very low volatilization degrees and remained in biochar after the gasification process, explaining the high ash content observed in BG biochars, compared to CS and OPS biochars. .

pH and pH_{PZC}

The three analyzed biochars exhibited very similar pH values in the alkaline region, between 9.8 and 10.9. The high pH range observed could be mainly related to the inorganic composition of the samples, and particularly to the presence of alkali and alkaline earth metals as principal inorganic constituents [38]. In fact, alkali and alkaline earth metals may be present in the biochars as carbonates and other compounds, including oxides, hydroxides, sulfates, and phosphates, which have a basic character [39, 40]. It is worth noting that no particular relationship was found between the pH of the analyzed biochars and their ash content.

Regarding the pH_{PZC}, the three biochars showed similar values in the acidic region, between 1.5 and 3, as presented in Fig. 1. The low pH_{PZC} observed indicates that the surface of the biochars is negatively charged in almost all the pH range, and then, the samples may favor the adsorption or retention of cations in soil applications. The pH_{PZC} determination plots are presented in Fig. S1 (supplementary material).

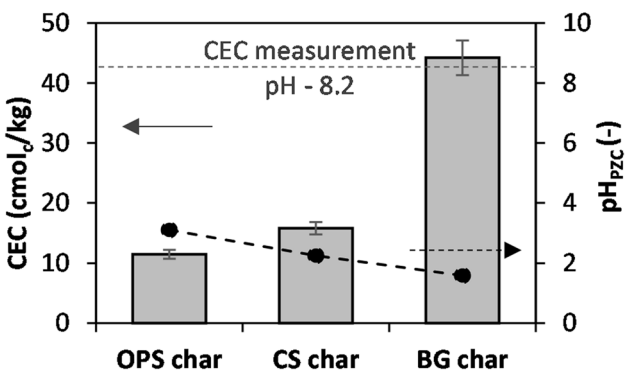


Fig. 1 Cation exchange capacity (CEC) and pH_{PZC} of the analyzed chars. The CEC capacity was measured at a pH of 8.2

Cation Exchange Capacity (CEC)

The analyzed samples showed CEC values between 10 and 45 $cmol_c$/kg, as observed in Fig. 1. BG biochar exhibited the highest value with 44.2 $cmol_c$/kg, followed by CS and OPS biochars with 15.8 and 11.5 $cmol_c$/kg respectively. Although CEC is not an intrinsic property of biochars and strongly depends on the measurement method used, the obtained results for the analyzed samples are in accordance with the values presented in the literature for numerous biochars from different feedstocks, between 6 and 150 $cmol_c$/kg [11, 17, 41–43].

Despite the fact that the three biochars were produced under the same gasification conditions, it is worth noting that the CEC observed for BG biochar is three times and four times higher than CS and OPS biochars respectively. These differences could be mainly related to the inorganic content of the samples, considering that BG biochar has the highest ash content (> 30%). From the SEM-EDX analysis performed, it was possible to determine that SiO_2 is one of the main mineral constituents of BG biochar, as presented in Fig. 2. SiO_2 may contribute in an important way to the CEC of this biochar, since this compound is negatively charged even at low pH, due to its very low pH_{PZC} value (~ 2.0) [44].

In the case of CS and OPS biochars, considering their low ash content (< 10%), the observed cation exchange capacity may be mainly associated with the oxygen-containing functional groups in their surface [18, 32]. In fact, steam gasification reactions can result in the chemisorption of oxygen and hydrogen in the biochar, creating oxygen-containing surface complexes that may impact the biochar surface charge and ion-exchange capacity. In particular, carboxyl groups (–COOH) have been reported as the main organic ion-exchange sites in biochars, which could modulate the release and uptake of nutrient ions in soils [10].

The existence of oxygen-containing functional groups (SOFG) in the surface of the analyzed biochars was confirmed by the thermal programmed desorption (TPD) results, summarized in Table 2. It is known that the CO_2 desorption is associated with the presence of carboxylic acids and lactones, while phenols, ethers, and quinones result in CO desorption. Also, carboxylic anhydrides decomposition is related to both CO and CO_2 release [29]. The detailed assessment of the contribution of each type of oxygen complex is presented in Fig. S2 and Table S1 (supplementary material). In this regard, the analysis of the CO and CO_2 desorption of biochars showed that their surface contains an important proportion of acidic SOFG, including mainly

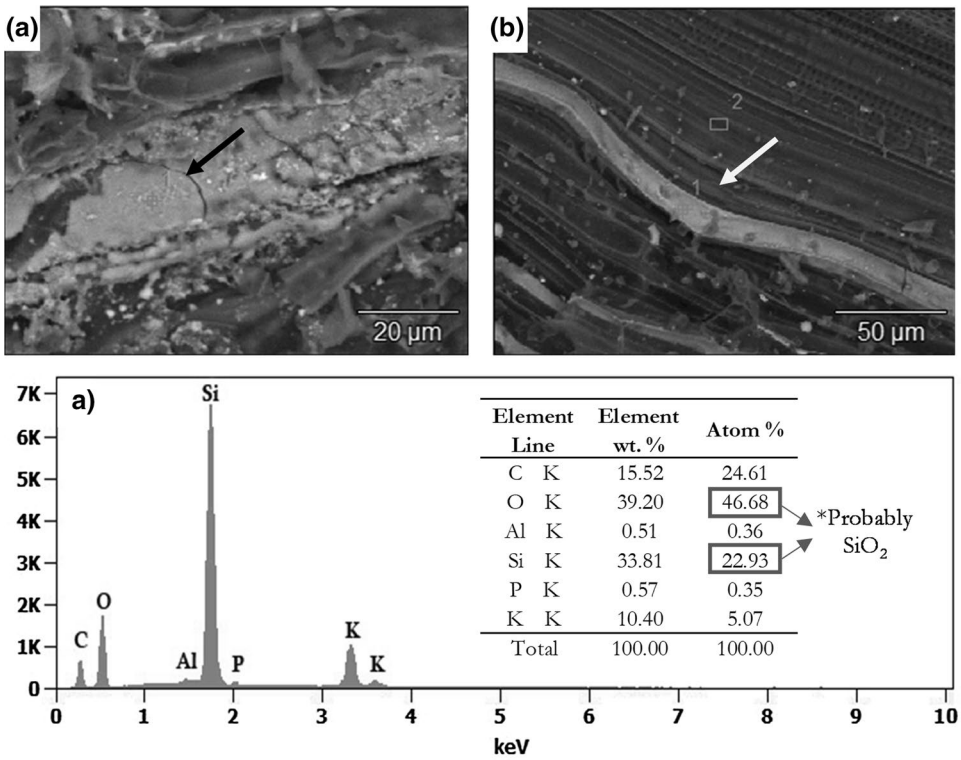


Fig. 2 SEM-EDX analysis of BG steam gasification chars

Table 2 Structure and surface characteristics of the analyzed biochars.

	CS biochar	BG biochar	OPS biochar
Pore structure			
S_{BET} (m^2/g)	1041.8 ± 12	807.7 ± 8	667.4 ± 10
S_{micro} (m^2/g)	898.9 ± 55	595.8 ± 25	550.0 ± 30
V_{micro} (cm^3/g)	0.34 ± 0.02	0.24 ± 0.01	0.25 ± 0.01
TPD CO and CO_2 desorption			
CO_2 (mmol/g)	0.84 ± 0.11	0.38 ± 0.08	0.15 ± 0.02
CO (mmol/g)	0.57 ± 0.05	0.56 ± 0.04	0.32 ± 0.02
Total (mmol/g)	1.41 ± 0.14	0.95 ± 0.10	0.48 ± 0.05
Carboxilic acid (mmol/g)	0.22	0.17	0.09
Phenols (mmol/g)	0.03	0.07	0.04
Peroxide (mmol/g)	0.12	0.05	0.02
Lactone (mmol/g)	0.49	0.16	0.05

carboxylic acids, peroxides, lactones, and phenols. It is worth noting that the presence of acidic groups in the biochar surface may be associated to the use of steam as reacting agent, during the gasification process [45, 46]. Moreover, the CO and CO_2 desorption observed for the analyzed biochars, and their calculated amount of SOFG are comparable to literature-reported values for biochars and activated carbons from different lignocellulosic precursors [10, 47, 48].

In particular, it can be observed that the total CO and CO_2 desorption measured for CS biochar is 1.5 and 3 times higher in comparison to the values obtained for BG and OPS biochars respectively. These differences indicate a greater amount of oxygen surface complexes in CS biochar in relation to OPS biochar, and may explain its higher CEC value. In fact, weakly acid carboxylic (–COOH) and phenolic (–OH) functional groups can dissociate and form negatively charged sites in the char surface (e.g. $–COO^-$, $–O^-$), which act as ion-exchange locations, contributing to the cation exchange capacity.

In this regard, several authors have reported that pyrolysis biochars produced at low temperature exhibit higher CEC values than high-temperature ones, as most of the oxygen-containing functionalities in the biochar surface are lost with the thermal treatment [8]. However, as the steam gasification process can result in the creation of oxygen-containing complexes in the char surface, the analyzed samples show comparable values to low-temperature pyrolysis biochars. In relation to this, the use of biochars in different kinds of soils has generally been related to the increase in their CEC and pH, providing benefits to soil fertility and crop yield [49, 50]. Considering that the reported pH and CEC values of different acidic soils are in the range of 4 to 6, and 5 to 20 $cmol_c$/kg respectively [11, 51–53], it can be said that steam gasification biochars may have an interesting potential to improve degraded soil properties.

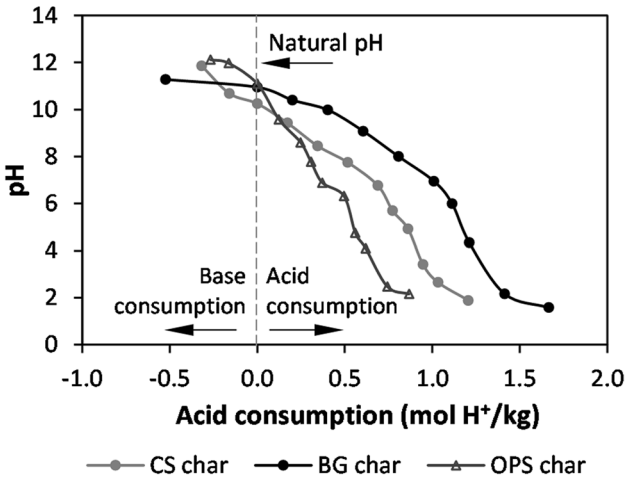


Fig. 3 Changes in biochar suspension pH as a function of acid-base titration

Acid Neutralization Capacity (ANC)

The acid neutralization capacity of biochars was analyzed to establish their capability to resist acidification. The acid-base titration curves for the three samples, presented in Fig. 3, indicate the amount of acid consumed by each biochar to decrease its pH to a value of 2. In accordance, a higher acid consumption is related to a greater buffering or acid neutralization capacity. In general, the ANC of biochar is defined as the quantity of acid (cmol/kg) required to shift the initial pH of the sample to a pH of 4 [54]. It may be attributed to the acidic oxygen-containing functional groups in the char surface, and its mineral content, existing either as discrete phases or associated with functional groups [11, 55].

In the case of the analyzed samples, with a basic natural pH, BG biochar showed the highest ANC, consuming 125 cmol/kg of H^+ protons, while CS and OPS values were 24% and 50% lower, with 95 cmol/kg and 62 cmol/kg respectively. Likewise, in all the analyzed pH range, from 2 to 12, BG biochars also showed the highest acid consumption, with 170 cmol/kg of H^+ protons, followed by CS and OPS, with 120 cmol/kg and 90 cmol/kg respectively.

The observed trend seems to be related to the inorganic content of the samples. More specifically, it can be noted that BG biochar has a considerably higher inorganic content (> 30% ash), in comparison to CS and OPS (< 10% ash), and then, exhibits the highest ANC. The differences observed between CS and OPS could be possibly related to the presence of a higher amount of oxygen-containing functional groups in CS biochar, as presented in Sect. 3.3.

To better understand this behavior, the release of minerals during the acid-base titration experiments was analyzed and compared for the three samples. From Fig. 4, it can be observed that in all cases, the total sum of K^+, Na^+, Ca^{2+}, and Mg^{2+} (base cations) released remained almost constant with the acid addition, while the soluble Si in the suspensions decreased with the pH. Despite the observed common trends, some differences were noticed between the three samples. In particular, the amount of base cations released by CS and BG biochars was approximately four times higher than OPS. Moreover, the Si release was higher for BG in almost all the pH range.

The base cations release indicates to the dissolution of alkali salts and oxides present in the biochar as discrete phases or associated with functional groups. The contribution of base cations release to the buffering capacity has been already described by several authors [10, 56], and may explain the fact that OPS biochar, with the lowest amount of K^+, Na^+, Ca^{2+} and Mg^{2+} released, is also the sample that exhibits the lowest proton consumption. Moreover, the greater Si release observed for BG in comparison to CS, may be related to its higher acid neutralization capacity. In fact, at high pH, soluble Si may be present in the solution as $H_3SiO_4^-$, which is transformed

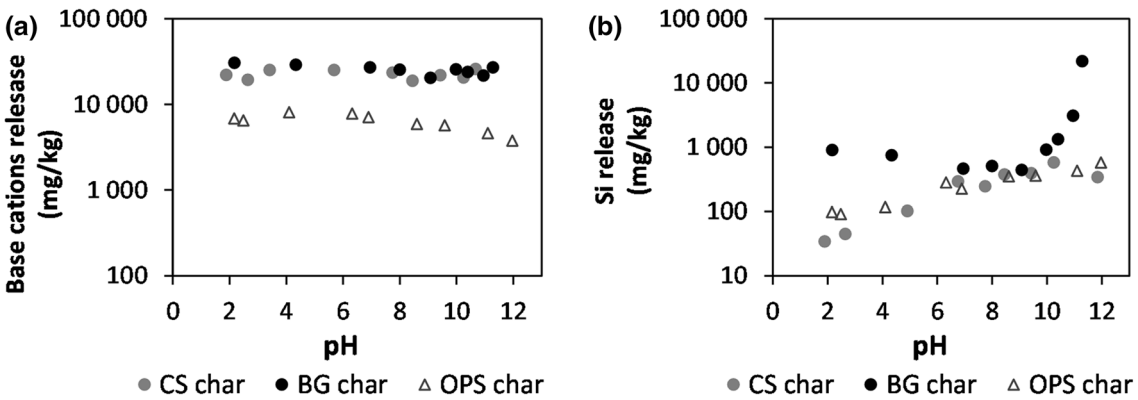


Fig. 4 Mineral release during the acid-base titration experiments. **a** Sum of base cations (K^+, Na^+, Ca^{2+} and Mg^{2+}), **b** Soluble Si

into H_4SiO_4 and precipitates when the pH decreases, consuming protons [57, 58].

These results suggest that inorganics play a primary role in the buffering capacity of the analyzed gasification biochars. The ANC of the analyzed samples is in accordance with some reported values in the literature for pyrolysis biochars from crop residues (100–200 cmol H^+/kg) [8, 10], showing the interesting potential of steam gasification biochars for acidic soil amendment applications.

pH-Dependent Mineral Release

The mineral leachability of biochars was also analyzed to determine their suitability to be used in environmental applications. The experimental results of a 48 hours leaching test

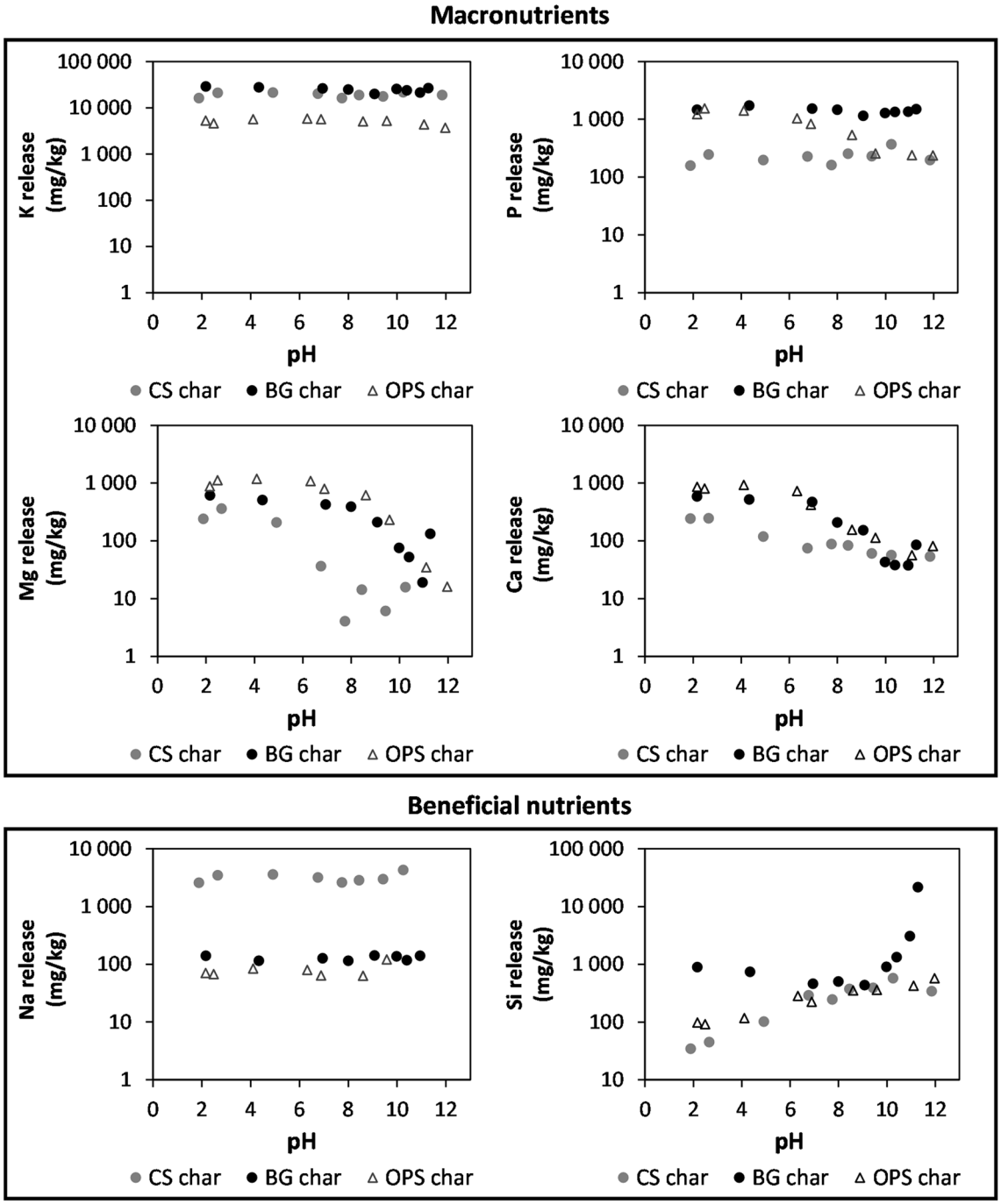


Fig. 5 Effect of pH on the K, Ca, Mg, Na, P, and Si release from gasification biochars

at pH values between 2 and 12, is presented in figure 5. In all cases, the release of a certain amount of K, P, Ca, Mg, Na, and Si from the biochar matrix was observed. In contrast, no significant leaching of Zn, Mn, Cu, Ni, or Fe was measured, even though these elements were identified in the biochar composition. Only a slight liberation of Mo was observed at a pH higher than 7.

The released amount of each element is in agreement with the mineral composition of the biochars and their ash content. For instance, the highest K concentration in the leaching solution was observed for BG biochar in all the pH range, considering that BG biochar has the highest K content. The same trend was observed for P, Ca, Mg, Na, and Si, for the three analyzed samples. Similar observations were reported by Ding et al. [59], suggesting that the composition and ash content of the biochars could give a first insight into their mineral leaching potential and nutrient value.

Nevertheless, it is worth noting that the recovered amount of minerals is not necessarily the total initial content present in the biochars. The mineral leachability may depend on different parameters, including the pH and redox potential of the surrounding environment, the occurrence forms and distribution of minerals in the biochar, and the biochar morphology [60]. For the analyzed samples, the observed solubility of minerals may be principally explained by their chemical form and bonding to the carbon matrix. For instance, the high release of alkali metals (K and Na) in all the pH range, may suggest that these elements are present in the biochar as soluble salts (e.g. carbonates, phosphates), hydroxides, or ion-exchangeable carboxylates. Moreover, P may be mainly present in the phosphate form (PO_4^{3-}), as it also shows high solubility in all the analyzed pH range [61]. In contrast, the limited leaching of alkaline earth metals (Mg and Ca) suggests that a fraction of these elements may be present as water-insoluble forms such as carboxylates or hydroxides. Similarly, transition metals compounds are generally insoluble (e.g. hydroxides), explaining the non-release of these minerals in a wide pH span. Only slight leaching of Fe, Ni, and Mn was observed (< 30 mg/kg) in highly acidic solutions, at pH values below 4.

To better understand the nutrient leaching potential of the analyzed samples, the amount released of each element is presented in Fig. 6, as a percentage of the total amount originally available in the biochar. A neutral pH (pH = 7) has been chosen as a reference. It can be observed that under the presented conditions, K, P, and Na are the minerals that exhibit the highest availability, with a recovery percentage from 40 to nearly 100%. The recovered fraction of K was above 85% for the three samples, indicating that this element is mostly present in the char structure as soluble K-containing salts [61]. In the case of Si, CS biochar showed a higher availability compared to BG and OPS. Considering that the solubility of amorphous silica is higher than that of

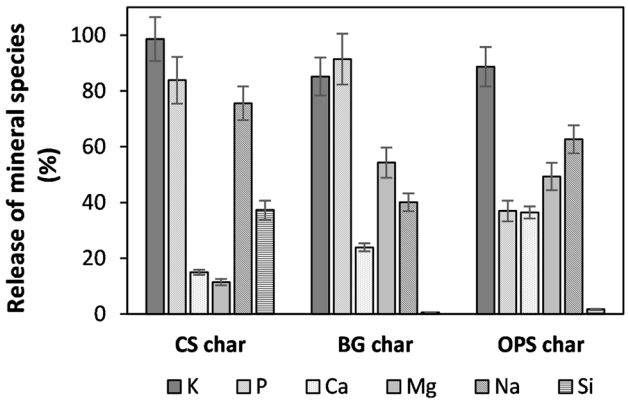


Fig. 6 Release percentage of mineral species from biochars at a pH = 7, during a 48 h leaching test with a liquid to solid ratio of 10 l/kg

crystalline silica [58], the leached amounts may correspond principally to the amorphous fraction present in biochars. Taking into account the considerably higher amount of Si in BG and OPS biochars in comparison to CS, the low leaching percentage observed for BG and OPS could indicate that an important amount of crystalline Si is present in their structure. Moreover, the high specific surface area and pore volume of CS biochar (Table 2), may also explain the higher release of minerals observed, compared to BG and OPS biochars. In fact, the biochar morphological structure may affect the accessibility of minerals, and consequently, their availability and release.

The results obtained in the present study are in accordance with some literature reported values, showing that the recyclability of N, K, and P is relatively high for biochars from different agrowastes [60, 62]. Nevertheless, the recovered percentages cannot be directly compared, as different solid to liquid ratios have been used for leaching studies, resulting in deviations caused by solubility and saturation limitations.

Agronomical Implications of Steam Gasification Biochar Properties

Steam gasification biochars from lignocellulosic agrowastes have shown high pH values, significant CEC and ANC, high specific surface area and pore volume, and non-negligible amounts of minerals. In accordance, their application to soils may be related to diverse potential agronomic beneficial effects.

The biochars high pH, as well as their significant ANC, suggest that these materials could be used for acidic soil amendment, increasing soil pH and preventing further acidification. Moreover, the CEC measured indicates that steam gasification biochars from agrowastes may increase the retention capacity of minerals in nutrient-poor and degraded

soils and enhance their availability and exchange when supplied by conventional procedures (e.g. traditional fertilizers).

Furthermore, the biochar mineral content may be related to an increase in nutrient availability in soils, improving both fertilizer efficiency and soil fertility. The observed mineral leaching behavior suggests that the analyzed samples may be a significant source of plant nutrients to soils. In the particular case of primary macronutrients (e.g. N, K, and P), the studied biochars showed a high K and P availability. For their part, secondary macronutrients such as Ca and Mg may also be supplied in some extent. Similarly, beneficial nutrients such as Na and Si showed a non-negligible release. In particular, Na is essential for the metabolism of some plants, and may improve the taste and texture of several crops (e.g. asparagus, barley, broccoli, beet) [63]. For its part, Si provides protection to plants from biotic and abiotic stress and may improve their strength and productivity [27]. It is worth noting that although low levels of Na in soils can be beneficial for certain plants, high concentrations of this element may be detrimental for other species (salt stress). In consequence, the choice of the most suitable biochar to be used in a particular application must take into consideration both the conditions of the targeted soil and the crop needs.

Considering that the recommended rates of biochar amendment in soils are between 5 and 50 ton char/ha [18, 64], gasification biochars could reduce the consumption of conventional fertilizers, notably regarding primary macronutrients (P and K). As an example, with a mean application rate of 10 tons/ha, and assuming similar conditions to those of the leaching tests performed in this work, the average available mineral quantities that could be supplied to the soil for plant uptake at a pH of 7, are presented in Table 3.

As observed, the amount of K released is significant for the three samples, as well as the P released by BG char. In this regard, considering the average macronutrient consumption reported for different crops, the analyzed gasification biochars could partially replace conventional K and P fertilizers. In particular, CS and BG biochars may supply up to 100% and 60% of the K and P needs of some low-input crops, like tomato, eggplant, lettuce, sweet corn, carrot, celery, or broccoli, throughout the growing season [65, 66].

Table 3 Average mineral release available for plant uptake with a rate of biochar amendment of 10 tons/ha

Inorganic elements		Average supply potential (kg/ha)		
		CS char	BG char	OPS char
Primary macronutrients	P	2.3	15.2	8.3
	K	201.0	259.8	56.5
Secondary macronutrients	Ca	0.7	3.1	5.7
	Mg	0.4	4.3	8.0
Micronutrients	Mn	0.0	0.0	0.2
	Mo	0.1	0.1	0.1
Beneficial nutrients	Na	31.7	1.3	0.6
	Si	2.9	4.6	2.3

In addition to the presented benefits to soil fertility, the high CEC of the analyzed biochars may be also important to the removal of inorganic contaminants from soils. In particular, the adsorption of cationic heavy metals could be favored, making them unavailable for leaching or plant uptake [22, 67]. Considering the low pH_{PZC} values of steam gasification biochars from agrowastes, heavy metal adsorption might be mainly associated to the electrostatic attraction between cationic metals and the negatively charged surface of biochar, as well as to the cation exchange between metal ions and mineral ions (K^+, Na^+, Ca^{2+}, and Mg^{2+}) [68–70]. In particular, BG biochars may be particularly suitable for heavy metals immobilization in soils, due to its high mineral content (with the presence of negatively charged SiO_2). It has been reported by different authors that the interactions between heavy metals and the biochar mineral content is the dominant factor in their sorption, in comparison to the SOFG effect [55]. Moreover, the high ANC of BG biochar could favor the increase of soil pH, and consequently, the formation of heavy metals non-soluble complexes (e.g. hydroxides, oxides, carbonates, and phosphates), turning those unavailable [44].

Finally, the morphology of the analyzed biochars, and specifically their high surface area and pore volume may also be associated with the improvement of the physical properties of soils, including their texture, bulk density, porosity, and water retention capacity. For instance, reported studies from several kinds of soils have shown that the use of porous biochar ($S_{BET} > 100\ m^2/g$) contributes to the increase of soil porosity by 2 to 40%, the reduction of the soil bulk density by 3 to 30%, and the increase of the soil water retention in almost 90% (depending on the soil properties and biochar application rate) [39, 71, 72]. In this regard, the three analyzed biochars, with surface area and pore volume above 667 m^2/g and 0.24 cm^3/g respectively, could improve the porosity and compaction of several soils, enhancing the transfer of water, nutrients and gases, and consequently, their agronomical performance.

Conclusions

Steam gasification biochars from different lignocellulosic agrowastes were analyzed in this work to determine their suitability to be used in soil amendment applications. Coconut shells (CS), oil palm shells (OPS), and bamboo guadua (BG) were selected as raw feedstocks considering their different macromolecular and inorganic composition.

The experimental results showed that the raw biomass composition was directly related to the biochar

physico-chemical properties and consequently, to the biochar potential to be used in environmental applications. In particular, the inorganic content and composition of the biochars showed a stronger impact on their properties for soil amendment and remediation, in comparison to their organic composition and morphology. BG biochar, the sample with the highest mineral content (> 30% wt), showed also the highest cation exchange capacity (45 $cmol_c$/kg), acid neutralization capacity (125 cmol H^+/kg), and mineral release at neutral pH. In contrast, in the case of low mineral content biochars (< 10% wt), higher CEC and ANC were mostly related to the presence of oxygen-containing functional groups in their surface, enhanced by the steam gasification process.

Considering that agricultural residues come from numerous sources and activities, the presented results usefully contribute to the comprehension of the relationship between the raw biomass characteristics, the physico-chemical properties of steam gasification biochars, and their expected performance in soil applications, opening a promising valorization pathway for these materials. Moreover, this work gives valuable insights for the proper selection of biochars from a particular feedstock, according specific soil requirements. The effect of the analyzed biochars in soils need to be confirmed under field conditions in the future.

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