



Novel K-enriched organomineral fertilizer from sewage sludge-biochar: Chemical, physical and mineralogical characterization

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ABSTRACT

Sewage sludge biochar (SSB) is a multi-nutrient fertilizer with very low K concentration. This study presents a novel K-enriched SSB fertilizer with the potential to increase K use efficiency by crops. The object of this work was therefore to evaluate the physical-chemical, morphological and mineralogical characteristics of a SSB organomineral fertilizer (OSSB) enriched with K. SSB was enriched with KCl and K₂SO₄ using three technological methods (granules, pellets and powders). The enrichment of SSB with K ensured a K₂O content about 75 times higher than the pure SSB. Organominerals in powder form had higher levels of total nitrogen, calcium, sulfur, phosphorus and higher pH than granules and pellets. The morphology and physical characteristics of enriched OSSBs were more influenced by the form of the fertilizer than by the source of K. In general, the enriched OSSBs are influenced by the quantities of feedstocks and the enrichment technology.

1. Introduction

Thermal treatment via pyrolysis is a technological alternative to transform sewage sludge (SS) into a multi-nutrient fertilizer. The solid product obtained by this process, called SS biochar (SSB), is free of pathogens and rich in carbon (C) and nutrients including nitrogen (N), phosphorus (P), calcium (Ca) and zinc (Zn) (Paz-Ferreiro et al., 2018). There are multiple feedstocks used for biochar production such as manure, wood and crop residues, and urban waste. Sewage sludge biochar is considered a nutrient-rich material, with the exception of potassium (K) (Figueiredo et al., 2018). In general, the last step of sewage treatment precipitates N and P. At the end of the SS treatment, >90% of the total P is precipitated as iron (Fe) and/or aluminum (Al) salts, which are insoluble in water, generating a SS rich in P (Tontti et al., 2016). Thus, pyrolysis has great potential to transform SS into a multi-nutrient fertilizer, especially rich in P and N (Fristák et al., 2018; Jassal et al.,

2015).

Potassium is eliminated as soluble salts together with the liquid effluent and is not incorporated into the solid SS (Kirchmann et al., 2016). Consequently, K content in SS ranges from 0.8 g kg⁻¹ up to 7.0 g kg⁻¹, averaging 2.0 g kg⁻¹ in dry matter (Figueiredo et al., 2018; Gwenzi et al., 2016; Tontti et al., 2016) which results in SSB with low K contents (Gwenzi et al., 2016; Sousa and Figueiredo 2016). Despite the increased K content due to the rise in pyrolysis temperature, it is not sufficient for the adequate supply of this nutrient to different crops (Fachini et al., 2021; Faria et al., 2018; Sousa and Figueiredo, 2016). This requires the complementation of K via mineral fertilization or by application of very high SSB doses.

Enriching SSB with K is an interesting alternative to make a complete fertilizer, with the potential to supply K to plants gradually and with greater efficiency. Recent studies have sought to develop mineral-enriched biochars (EBs) to act as slow-release fertilizers (Jassal et al.,

Abbreviations: SS, Sewage sludge; SSB, Sewage sludge biochar; EB, Enriched biochar; OMBC, Organomineral biochar; OSSB, Organomineral fertilizer from sewage sludge biochar; IBI, International Biochar Initiative regulation; OC, Organic carbon; TC, Total carbon; TN, Total nitrogen; FA, Fulvic acid; HA, Humic acid; HU, Humin; SA, Specific surface area; PV, Pore volume; HS, Humic substances; PMV, Micropores volume; SEM, Scanning electron microscopy; XRD, X-ray diffraction; EDX, Energy dispersive X-ray spectrometry; ICDD, International Center Diffraction Data; AD, Apparent density; PD, Particle density; VM, Volatile matter; FC, Fixed carbon; SOM, Soil organic matter; BET, Brunauer–Enmett–Teller Model.

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2015), balancing and enabling the supply of nutrients to plants (Darby et al., 2016; Farrar et al., 2018). Mixtures of biochars with other organic and/or mineral sources can give rise to EBs (Chia et al., 2014; Gondek et al., 2018) or organomineral biochar (OMBCs) (Farrar et al., 2018; Nguyen et al., 2017).

Enriched biochars can be applied at low rates and have a higher efficiency than pure biochars, mineral or organic fertilizers (Farrar et al., 2018; Nguyen et al., 2017). Due to the high porosity and large surface area, as well as the interaction of the enriched element with the biochar surface, EBs can retain nutrients and act as a slow-release fertilizer (Schmidt et al., 2017). Changes in several physical and chemical characteristics of EBs and OMBCs have already been reported compared to their raw materials. For instance, the enrichment of wheat straw biochar with mineral salts resulted in increased levels of sulfur (S) and magnesium (Mg) and reduced pH compared to the pure biochar (Gondek et al., 2018). Increases of 2.7 and 56.6 times in N and P levels, respectively, were observed after the enrichment of wood biochar with mineral and organic sources (Blackwell et al., 2015). Larger pores coated with P, K, Ca and Mg were observed by Farrar et al. (2018) in manure and wood OMBC. On the other hand, the co-pyrolysis of SS with different organic biomass resulted in biochars with less surface area and porosity compared to pure SSB (Huang et al., 2017).

Studies with EBs and OMBCs are relatively recent. Therefore, there is a wide variation in the methods used to obtain the final product (Farrar et al., 2018; Nguyen et al., 2017). Granulating and pelletizing biochars are the most common processes which have been used to minimize dust production, and consequently reduce respiratory problems caused by biochar application in the form of powder (Vincevica-Gaile et al., 2019). In addition, these products can facilitate the application of biochar in the field. Another advantage of producing EBs and OMBCs is that these fertilizers can be enriched with specific nutrients and adapted according to the requirements of the crop (Farrar et al., 2018). In general, soils of tropical regions have low contents of available nutrients. In Brazil, the most used formula is 4–14–8 (NPK) and high doses of this fertilizer are applied because of the low use efficiency of P and K fertilizers (Lopes and Guilherme, 2016). Additionally, EBs reduce the high doses of biochars that may cause soil pollution, hindering the adoption of biochar technology by farmers.

There is still a lack of information on the enrichment of SSB with soluble K sources using different technologies such as granulation and pelletizing. Contrasting results on the effectiveness of organomineral fertilizers could be related to the physical formulation (e.g., powder, granular, pellet), physicochemical properties and composition of the mineral and organic sources used (Frazão et al., 2019). Furthermore the physical formulation can affect the efficiency of storage, handling and application, as well as the plant responses. For instance, Sakurada et al. (2016) reported significant differences between granular and pelletized organomineral fertilizers applied to maize. However, the characterization of OMBCs has been poorly performed in most studies, which compromises the interpretation of effectiveness results behind the reactions of OMBCs in the soil. Therefore, studies on this subject are relevant for a better comprehension of the agronomic effectiveness of OMBCs, which allow for future adjustments in terms of fertilizer formulation.

In this context, the present study sought to evaluate the physical, chemical, morphological and mineralogical characteristics of organomineral fertilizer from SSB (OSSB) enriched with two K sources and different physical forms. It was hypothesized that all OSSBs enriched with K sources have similar compositions but have distinct physical and mineralogical properties, depending on the physical form and K source used.

2. Materials and methods

2.1. Preparation of sewage sludge biochar (SSB)

The SSB was produced from SS samples collected at the Melchior

wastewater treatment plant, belonging to the Environmental Sanitation Company of Brasília, DF, Brazil. This wastewater treatment plant utilizes a tertiary treatment system, in which sewage decomposition is carried out in an anaerobic up-flow reactor (RAFA). In this type of system, nutrients such as P and N are removed from the liquid effluent by a coagulation process using aluminum salts. Therefore, these nutrients remain in the final SS biomass.

For SSB preparation, SS samples were air-dried (to approximately 10% moisture content), passed through a 4 mm sieve and then pyrolyzed at 300 °C. Based on our previous study (Figueiredo et al., 2018), considering all variables together, the biochar produced at 300 °C showed the greatest nutrients availability. Pyrolysis was performed in a muffle furnace (Linn ElektroTherm, Eschenfelden, Germany) at a mean temperature increase rate of 2.5 °C min⁻¹ and residence time of 5 h as described by Figueiredo et al. (2018). The furnace was equipped with a mechanism to prevent oxygen flow (via forced draft fan, helping gas and oil vapors exit the furnace).

The physical and chemical characteristics of SS and SSB are shown in Table 1. The methods used in this characterization are described in our previous work (Figueiredo et al., 2021).

2.2. Experimental setup and fertilizer production

The experiment was setup in a completely randomized design with 2x3 factorial treatments (2 K sources and 3 physical forms) and three replications, totaling 6 treatments. The K sources were KCl and K₂SO₄, whereas the physical forms were powder, granule and pellet. Thus, the treatments tested were: 1) OSSB-KCl powder; 2) OSSB-KCl pellet; 3) OSSB-KCl granule; 4) OSSB-K₂SO₄ powder; 5) OSSB-K₂SO₄ pellet; and 6) OSSB-K₂SO₄ granule.

Organomineral fertilizers (treatments) were produced from a physical mixture of SSB, K sources and additives (e.g., binding agent). The feedstocks were mixed to obtain a final mass of 1.0 kg of each organomineral fertilizer. Considering the values of total nitrogen (TN) and P₂O₅ in SSB, the final K concentration in OSSBs was fixed at 3% to meet the legal requirements, whose sum of NPK must be >10% (Brazil, 2009). Thus, 50.0 and 59.0 g of KCl and K₂SO₄ were added, respectively, to supply 3% K₂O. As a binding agent, 65 g of pre-gelatinized starch was also added to produce granules and pellets. As a source of N and P, SSB was added to complete 1.0 kg of the formulation.

The SSB and K sources were crushed in an industrial device (Philco PLQ 1400), and later passed through a 0.500 mm mesh sieve. The formulations SSB + KCl + starch (OSSB-KCl) and SSB + K₂SO₄ + starch (OSSB-K₂SO₄) were subjected to the granulation and pelleting processes. Additionally, powder mixtures of raw materials without starch were studied as OSSB in a powder form.

The pellets were produced in a laboratory pelletizer (ENG-MAQ, model ENG 0200 V, São Paulo, Brazil). For each 1.0 kg batch of OSSB, 140 mL of distilled water was used to facilitate agglutination of the raw materials. At the end of this process, pellets with a diameter of 6 mm and 1 cm in length were produced. After this process, the pellets were dried in an oven at 65 °C for 24 h.

The granules were produced in a laboratory granulator composed of a cylindrical tray measuring 7 cm high by 36 cm in diameter, inclined at an angle of approximately 70°, coupled to a motor operating at 40-rpm. During granulation, distilled water was also added by spraying it on the raw material. Afterward, the granules were passed through a set of 3 sieves with different meshes, according to the sequence: 4 mm, 2 mm and 1 mm. The granules >4 mm and smaller than 1 mm were crushed again and granulated to obtain granules between 1.0 and 4.0 mm. Finally, the granules were dried in an oven at 65 °C for 24 h.

Table 1
Characteristics of sewage sludge (SS) and sewage sludge biochar (SSB).

Property ^a	SS	SSB		
		(This work)	(Previous works) ^c	Reference
pH (CaCl ₂)	6.4 ± 0.05	6.5 ± 0.02	7.0	[1,2,7,8]
Moisture content (%)	10.4 ± 0.11	8.4 ± 0.03	–	–
Volatile matter (%)	55.7 ± 0.32	47.2 ± 0.49	32.1	[2,5,10,12]
Ash (%)	32.4 ± 0.17	38.1 ± 0.18	61.2	[3,4,10–13]
Fixed carbon (%)	1.5 ± 0.19	6.3 ± 0.64	8.7	[10,12,13]
OC (%)	18.3 ± 0.11	18.3 ± 1.06	–	–
TC (%)	25.1 ± 0.17	27.1 ± 0.08	25.8	[1–11]
TN (%)	3.9 ± 0.17	4.3 ± 0.13	4.4	[1–12]
C/N	6.4 ± 0.11	6.3 ± 0.17	6.4	[4,6]
P ₂ O ₅ (%)	4.7 ± 0.07	5.5 ± 0.08	4.8	[2,5–7,10–12]
K ₂ O (%)	0.05 ± 0.01	0.04 ± 0.01	0.05	[2,4,6,7,10–13]
Ca (g kg ^{−1})	6.0 ± 0.03	6.9 ± 0.04	12.9	[2,10–13]
Mg (g kg ^{−1})	1.40 ± 0.2	1.54 ± 0.01	3.8	[2,10–13]
S (%)	1.30 ± 0.4	1.62 ± 0.01	1.89	[2,8,10,11]
Fe (g kg ^{−1})	17.5 ± 1.06	20.0 ± 2.1	12.7	[10]
B (mg kg ^{−1})	26.4 ± 3.0	31.2 ± 1.1	–	–
Mn (mg kg ^{−1})	88.6 ± 4.2	100.0 ± 11.3	360.5	[4,6]
Zn (mg kg ^{−1})	414.2 ± 19.1	453.9 ± 2.1 ^b	1.308	[2,7–10,12,13]
Cu (mg kg ^{−1})	88.1 ± 5.5	100.0 ± 2.3 ^b	250.6	[3,4,7,8,12,13]
Co (mg kg ^{−1})	9.7 ± 0.6	11.9 ± 1.9 ^b	16.0	[2]
Mo (mg kg ^{−1})	33.9 ± 0.1	42.4 ± 2.5 ^b	–	–
Cd (mg kg ^{−1})	18.1 ± 0.7	19.3 ± 3.5 ^b	2.5	[3,4,8]
Cr (mg kg ^{−1})	47.3 ± 2.7	53.0 ± 0.1 ^b	59.8	[1,4,7,8,12]
Ni (mg kg ^{−1})	14.4 ± 1.3	28.4 ± 0.6 ^b	29.6	[1,7,8,12,13]
Pb (mg kg ^{−1})	414.2 ± 19.1	148.5 ± 0.7 ^b	103.5	[3,4,7,8,12,13]
FA (g kg ^{−1})	35.0 ± 0.85	33.7 ± 0.82	–	–
HA (g kg ^{−1})	14.9 ± 0.55	9.3 ± 1.60	–	–
HU (g kg ^{−1})	179.1 ± 0.58	229.4 ± 8.08	–	–
SA (m ² g ^{−1})	21.9	27.8	22.5	[1–3,5,8,10–13]
PV (cm ³ g ^{−1})	0.096	0.102	0.100	[3,8,12]

^a : average values ± standard deviation (n = 3); OC = organic carbon; TC = total carbon; TN = total nitrogen. FA: fulvic acid; HA: humic acid; HU: humin; SA: specific surface area; PV: pore volume. ^b: heavy metal contents are below the maximum permitted by the International Biochar Initiative regulation (IBI, 2015). ^c: mean values of SSB found in previous studies. ¹Agrafioti et al. (2013); ²Chagas et al. (2021); ³Mierzwa-Hersztek et al. (2018); ⁴Tian et al. (2019); ⁵Gonzaga et al. (2018); ⁶Jafari Tarf et al. (2021); ⁷Khanmohammadi et al. (2015); ⁸Khan et al. (2015); ⁹Yuan et al. (2013); ¹⁰Zhang et al. (2015); ¹¹Figueiredo et al. (2018); ¹²Yuan et al. (2015); ¹³Méndez et al. (2012).

2.3. Physical, chemical, mineralogical and morphological characterization of sources

2.3.1. Proximate analysis

Enriched biochar samples were passed through a 0.250 mm mesh sieve. For proximate analysis, moisture, volatile matter, fixed carbon and ash contents were determined by heating the samples in a muffle

furnace (Linn-ElektroTherm, model KK 260 SO 4060) according to the method proposed by ASTM international (2013).

2.3.2. Elemental analysis

Total carbon (TC) and TN were determined using an elemental analyzer (Euro EA3000 Elemental Analyser, Milano, Italy) equipped with a thermal conductivity detector. Samples (approximately 5 mg) were placed in an auto-injector for analysis.

2.3.3. pH and nutrients

After drying, grinding and sieving through a 0.500 mm mesh sieve, pH and macronutrients contents of the samples were determined. The pH was determined in a 0.01 M CaCl₂ solution, using a 1:5 (w/v) solid: solution ratio suspension (USEPA, 1996). For the extraction of macronutrients (Ca, Mg and S), samples were subjected to acid digestion according to USEPA 3050B (USEPA, 1996), and quantified by ICP-OES (ICPE-9000, Shimadzu, Japan). The concentration of P was determined by the molybdovanadophosphoric acid colorimetric method (Brasil, 2017), following nitric-perchloric extraction. The P concentration was estimated in a spectrophotometer at 400 nm (Automatic Digital Spectrophotometer SP 22, China). The concentration of K was determined by flame photometry (Brasil, 2017).

2.3.4. Organic carbon and humic substances

The organic carbon (OC) content was determined by the volumetric method of potassium dichromate (Walkley and Black, 1934). Determination of humic substances (HS) was performed according to the differential solubility technique (Swift, 1996). Carbon levels of fulvic acid (FA), humic acid (HA) and humin (HU) were estimated by dichromatometry according to Yeomans and Bremner (1988).

2.3.5. Surface area and pore volume

The surface area (SA), pore volume (PV) and micropores volume (PMV) were determined by N₂ adsorption isotherms at − 196.2 °C using a surface area analyzer, NOVA 2200 (Quantachrome Corp., Boynton Beach, FL, USA). Values were estimated automatically by the software Quantachrome NovaWin®, using the BET (Brunauer, Emmett and Teller) equation.

2.3.6. Scanning electron microscopy (SEM) images

To obtain SEM images, samples were attached to stubs with carbon adhesive tape and then metalized with an electrically conductive thin gold film by the sputtering method. Analyses were performed using a microscope of the brand Jeol KAL-70001F (Waltham, Massachusetts, USA).

2.3.7. X-ray diffraction (XRD) and energy dispersive X-ray spectrometry (EDX) analysis

The XRD analysis was carried out on a diffractometer (D8 Focus, Bruker, Germany). Powder XRD patterns were obtained using monochromatic Cu Kα radiation at 40 kV, 30 mA, with 2θ between 10 and 70°. The peak areas identified for the different minerals were compared with XRD patterns of standard minerals compiled by the ICDD (International Center Diffraction Data). Samples were also submitted for energy dispersive EDX analysis. EDX patterns were obtained using an EDX 720HS (Shimadzu) spectrometer. For both analyses (XRD and EDX) whole samples were used.

2.3.8. Apparent density and particle density

The apparent density (AD) of the OSSB was determined according to British (1995). Cylinders measuring 50 cm³ were filled with OSSB samples and the calculation of AD was performed according to equation (1) (Eq. (1)):

$$AD = w/v \quad (1)$$

where, AD = apparent density (g cm^{−3}); w = weight of

organomineral needed to fill the cylinder (g); v = volume of the cylinder (cm^3).

The particle density (PD) of organominerals (granules and pellets) was also determined according to the British Standard Method (British, 1995). The individual volume of 10 granules and 10 pellets of the same granulometry were calculated using a digital caliper. Thereafter, the mass of each material (granule and pellet) was determined on a precision balance. Subsequently, calculation of PD was performed according to equation (2) (Eq. (2)):

$$PD = w/v \quad (2)$$

where, PD = particle density of the granule or pellet (g cm^{-3}); w = weight of the granule or pellet (g); v = volume of the granule or pellet (cm^3).

2.4. Statistical analyses

Data normality was validated by the Shapiro-Wilk test ($\alpha = 0.05$) and the homogeneity of variance by Bartlett's test. A two-way analysis of variance (ANOVA) and the Tukey posthoc honest significant difference test were used to compare treatment means at a 5% level of significance. All statistical analyses were performed using the XLSTAT software (Addinsoft, 2013).

3. Results and discussion

3.1. Chemical and mineralogical characterization of OSSBs

3.1.1. Proximate analysis and pH

The OSSB pH values were affected by the interaction between K sources and forms ($P < 0.05$; Table 2). In general the OSSB powder showed higher pH than pellets and granules, and OSSB- K_2SO_4 pellets presented values between the granules and powder. The addition of water in the granulation and pelletization processes may have solubilized part of the mineral fertilizer (KCl or K_2SO_4), promoting ion exchange between the fertilizers and the SSB. Thus, there may have been a change in pH of the medium due to the marked increase in concentration of ions supplied by fertilizers to the microenvironment, resulting in the displacement, release or solubilization of other ions of an acid character (Du et al., 2010).

Although KCl has a neutral acidity/basicity index (Coelho, 1994), the

Table 2

Volatile matter (VM), pH, ash, fixed carbon (FC), total C and N contents of K-enriched organomineral fertilizers.

Form	Source							
	OSSB-KCl		OSSB- K_2SO_4					
	pH (CaCl_2) ¹							
Granule	5.7	b B	5.8	c A				
Pellet	5.7	b B	6.1	b A				
Powder	6.6	a A	6.6	a A				
Source	VM (%)	Ash (%)	FC (%)	TC (%) ²	TN (%) ³			
OSSB-KCl	49.7	a	39.6	a	4.2	a	25	a
OSSB- K_2SO_4	50.6	a	39.6	a	3.2	b	25	a
Form								
Granule	51.3	a	39.7	ab	2.1	b	25	a
Pellet	52.3	a	38.6	b	3.9	b	25	a
Powder	47.0	b	40.6	a	5.1	a	24	a

Means followed by equal letters, uppercase in the row and lowercase in the column, do not show statistical differences according to the Tukey test ($P < 0.05$). Reference values (range) of various organomineral fertilizers reported in literature: ¹: pH = 4.3 – 7.9 (Olowokere et al., 2013; El-Mageed and Semida, 2015; Gurgel et al., 2015; Frazão et al., 2019); ²: TC = 20 – 40 % (Mazeika et al., 2016; Adebayo et al., 2017; Frazão et al., 2019); ³: TN = 0.45 – 13% (Antille et al., 2013; El-Mageed and Semida, 2015; Gurgel et al., 2015; Adebayo et al., 2017; Frazão et al., 2019).

OSSB-KCl, compared to OSSB- K_2SO_4 , resulted in lower pH values in all forms (except in powder form). In addition, KCl has a greater solubility (300 g L^{-1}) than that of K_2SO_4 (110 g L^{-1}) at 20°C (Coelho, 1994). Thus, the same amount of water added in the granulation and pelletization process can promote greater KCl solubilization, resulting in a pH reduction for OSSB-KCl in the form of granules and pellets compared to OSSB- K_2SO_4 .

Volatile matter, ash and fixed carbon were not influenced by the interaction between K sources and forms ($P > 0.05$; Table 2). No differences in volatile matter were found between OSSB-KCl and OSSB- K_2SO_4 ($P > 0.05$; Table 2). OSSBs in the form of granules and pellets showed a higher value of volatile solids than the powder form, probably because corn starch was used as a binding agent. According to Novak et al. (2009), high temperatures contribute to the dehydration of hydroxyl groups in starch, which may have resulted in greater volatilization of C, hydrogen (H) and oxygen (O) in organomineral fertilizers formed with the addition of this binder. No differences in ash contents were found between K sources ($P > 0.05$; Table 2). Powder OSSBs had higher ash contents than pellets. Likewise, OSSBs in powder form had the highest fixed carbon levels. The K source also influenced the FC content, where OSSB-KCl had a higher FC than OSSB- K_2SO_4 , probably due to the higher percentage of SSB used in the production of OSSB-KCl.

3.1.2. Elemental composition

The TC contents in the OSSBs were similar between sources of K and physical forms of the fertilizers ($P > 0.05$). In general, the TC contents for all OSSBs were close to 25% (Table 2). The levels of TN were affected only by the physical form of the fertilizers. The only source of N used in the production of organomineral fertilizers was SSB. Therefore, because powdered fertilizers have a higher percentage of SSB, they had a higher TN content compared to granules. In general, all fertilizers had on average 3.3% of TN. This value is above the levels typically found in enriched biochars and organomineral fertilizers obtained from different raw materials such as wood, manure, wheat straw and bamboo that have a TN content ranging from 0.94 to 2.14% (Blackwell et al., 2015; Chia et al., 2014; Darby et al., 2016; Farrar et al., 2018; Frazão et al., 2019; Gondek et al., 2018; Nguyen et al., 2017; Olowokere et al., 2013).

3.1.3. Macronutrients composition

The Ca content was influenced by the interaction between K sources and fertilizer form ($P < 0.05$; Table 3). The OSSB powder showed higher Ca contents than pellets and granules. Because the fertilizers KCl and K_2SO_4 do not have Ca in their constitution, the Ca present in organomineral fertilizers comes only from SSB. Organomineral fertilizers in powder form showed higher Ca contents than granules and pellets, resulting from the higher proportion of SSB in their composition.

Only the fertilizer form had a significant effect on the Mg and total P_2O_5 contents in organominerals (Table 3). Of the total organomineral mass, 88.5 and 87.6% of SSB were used for enrichment with KCl and K_2SO_4 , respectively, resulting in similar values of Mg and total P_2O_5 between the sources of K. Powdered organominerals showed the highest contents of Mg and total P_2O_5 compared to the granules and pellets which showed no differences amongst each other. For enrichment of the organomineral powder, a higher percentage of SSB was used in the final mass, contributing to a higher content of these nutrients. In general, SSB has a higher P content than biochars from other raw materials (Kim et al., 2018), representing a good option for the composition of organominerals. It is currently well known that SSB is a source of P for crops, potentially replacing soluble mineral fertilizers (Faria et al., 2018; Fachini et al., 2021). As a fertilizer, SSB can supply from 4.5 to 7.2 times more P to soil than conventional P fertilizers (Chagas et al., 2021). Additionally, the P content in maize leaves cultivated in soil amended with SSB was around 67% higher compared to chemical fertilizers.

Sulfur contents were influenced by the sources and form ($P < 0.05$; Table 3). Regardless of the fertilizer form, the highest S levels were found in OSSB- K_2SO_4 (Table 3). When enriched with K_2SO_4 , the S levels

Table 3

Macronutrients and organic carbon (OC) in K-enriched organomineral fertilizers.

Form	Source											
	OSSB-KCl		OSSB-K ₂ SO ₄									
	Ca (g kg ⁻¹)											
Granule	5.5			b B			6.2			b A		
Pellet	5.5			b A			5.8			b A		
Powder	7.0			a A			6.6			a A		
Source	Mg (g kg ⁻¹)		S (g kg ⁻¹)		K ₂ O (%)		P ₂ O ₅ (%)		Sum NPK		OC (g kg ⁻¹)	
OSSB-KCl	14.5	a	1.3	b	3.0	a	5.3	a	11.3	a	178	a
OSSB-K ₂ SO ₄	14.1	a	2.2	a	3.0	a	5.2	a	11.6	a	173	a
Form												
Granule	13.8	b	1.6	c	3.0	a	5.1	b	11.2	a	175	ab
Pellet	14.2	b	1.7	b	3.0	a	5.1	b	11.4	a	194	a
Powder	15.0	a	1.9	a	3.0	a	5.4	a	11.7	a	158	b

Means followed by equal letters, uppercase in the row and lowercase in the column, do not show statistical differences according to the Tukey test ($P < 0.05$).

in organomineral fertilizers were higher because S came from both SSB and K₂SO₄. The KCl source resulted in organomineral fertilizers with an S content similar to the pure SSB, 1.6 g kg⁻¹ (Table 1). Powdered organomineral fertilizers, regardless of the K source, presented higher S levels than granules and pellets, resulting from the higher percentage of SSB in the composition of the organomineral fertilizer.

The K₂O contents were similar between organomineral fertilizers regardless of the source of K and the physical form of the fertilizer ($P > 0.05$; Table 3). The enrichment of SSB with K guaranteed a 75-fold increase in K₂O content of OSSBs compared to pure SSB (Table 1). According to the percentage added in the production of these fertilizers, all organomineral fertilizers presented 3% K₂O. Powdered organominerals had a higher SSB percentage in the final mass. However, the low content of K₂O in the SSB (0.04%) did not increase the content of this nutrient in powder OSSBs compared to granules and pellets. These results prove the efficiency of enriching SSB with K sources to supplement the low K supply when using the pure SSB.

3.1.4. X-ray spectra by energy dispersive spectrometry

As expected, the most prominent effect of SSB enrichment was the observed increase in K levels (Fig. 1.). Potassium peaks (Fig. 1) with an increase of 6.8 and 7.2 times, respectively, for the enrichment of the SSB with KCl and K₂SO₄, compared to the pure SSB (Data not shown), prove the efficiency of enrichment with K sources to supplement the deficiency of this nutrient in the SSB.

The intensities of the Ca peaks were similar among K sources, with averages of 0.27 and 0.29 cps/uA for KCl and K₂SO₄, respectively. As a result of the higher SSB composition, powdered organomineral fertilizers, regardless of the K source, showed Ca peaks with an intensity of 0.34 cps/uA, similar to that of SSB (Data not shown). On average, the characteristic peaks of P for KCl (1.8 cps/uA) and K₂SO₄ (1.9 cps/uA) were similar to those found in the SS and SSB (Data not shown). These results prove that pyrolysis preserves or increased P concentration, representing a desirable feature for the production of sustainable fertilizers.

The OSSB-K₂SO₄ showed more intense S peaks than OSSB-KCl. As expected, peaks of Cl were observed only in OSSB-KCl due to the presence of Cl in the KCl fertilizer. The peaks of Fe, Al and Si are due to the presence of these elements in the SS and consequently in the SSB. X-ray photoelectron spectroscopy spectra obtained by Shen et al. (2018) proved that the main elementary components in the pure SSB were Fe, Al and Si. This composition results from inorganic compounds such as Si, and Fe and Al salts in sewage sludges (Yuan and Dai, 2015).

3.1.5. X-ray diffraction (XRD) spectra

Fig. 2. shows the XRD spectra of organomineral fertilizers enriched with KCl (Fig. 2A) and K₂SO₄ (Fig. 2B). In general, there is a wide range of typical peaks that indicate a wide variety of mineral components. Like SSB, organomineral fertilizers showed an increase in peaks in the range

of $2\theta = 20^\circ$ to 30° , indicating C in graphite-like amorphous structures (Hsu et al., 2019). In addition, all organomineral fertilizers showed peaks that indicate the presence of quartz (SiO₂), gibbsite [Al(OH)₃], variscite (AlPO₄), calcite (CaCO₃) and dolomite [CaMg(CO₃)₂], confirming previous studies (Liew et al., 2004; Shen et al., 2018; Wang et al., 2018). The mineralogical composition of the fertilizers was very similar to the pattern observed in pure SSB (data not shown). On the other hand, after enrichment peaks at 28° , 41° and 50° were seen in the OSSB-KCl (Fig. 2A), indicating the presence of silvite (KCl) according to previous studies (Wang et al., 2018). In the OSSB-K₂SO₄ (Fig. 2B), peaks close to 16° , 30° and 40° confirmed the presence of the arcanite mineral (K₂SO₄) (Francello et al., 2019; Kim et al., 2012).

Enrichment with K did not change the mineralogical composition of OSSBs except for the silvite and arcanite minerals from K sources (KCl or K₂SO₄). More intense peaks of quartz are observed in organomineral fertilizers in the powder form due to the higher percentage of SSB in the final mixture formulation.

3.1.6. Organic matter and humic substances

Humic fractions of the organominerals were not affected by interaction of the K source and the physical form of the fertilizer, nor by the isolated factors (Data not shown). The humic fractions values ranges from 32.2 g kg⁻¹ up to 33.9 g kg⁻¹ for FA, 10.4 g kg⁻¹ up to 11.5 g kg⁻¹ for HA and 177.6 g kg⁻¹ up to 220.2 g kg⁻¹ for HU. There was an effect only of the fertilizer form on the OC content. SSB and starch, used in granules and pellets, were the sources of OC in organomineral fertilizers. Because they have similar percentages of SSB and starch, OSSB-KCl and OSSB-K₂SO₄ showed similar OC contents. Organic C concentrations in organomineral fertilizers were similar to those of SSB and SS, approximately 18.3% for both (Table 1). Pellets showed a higher OC content than the powder form. These results may be related to the addition of starch in the granulation and pelletization processes.

The high OC concentration in organomineral fertilizers (about 18%) represents an essential substrate for soil microbial activity and the processes of immobilization and mineralization of nutrients. Although the increase in soil C contents after applying biochars is already well established (Yang et al., 2017; Yue et al., 2017), there are still doubts about the effect of using biochar-based organomineral fertilizers on soil C stocks. Therefore, OSSB, in addition to the supply of nutrients, can contribute over time to the increase in soil organic matter (SOM) fractions, increasing soil biota, aggregate stability and formation of humic substances.

3.2. Physical and morphological characterization

3.2.1. SEM images of K-enriched organomineral fertilizers

In Fig. 3 it is possible to visualize the different structures of the granulated, pelletized and powdered OSSBs and differentiate their pore-filled surfaces. Fig. 3A and 3G show the joining of several particles of

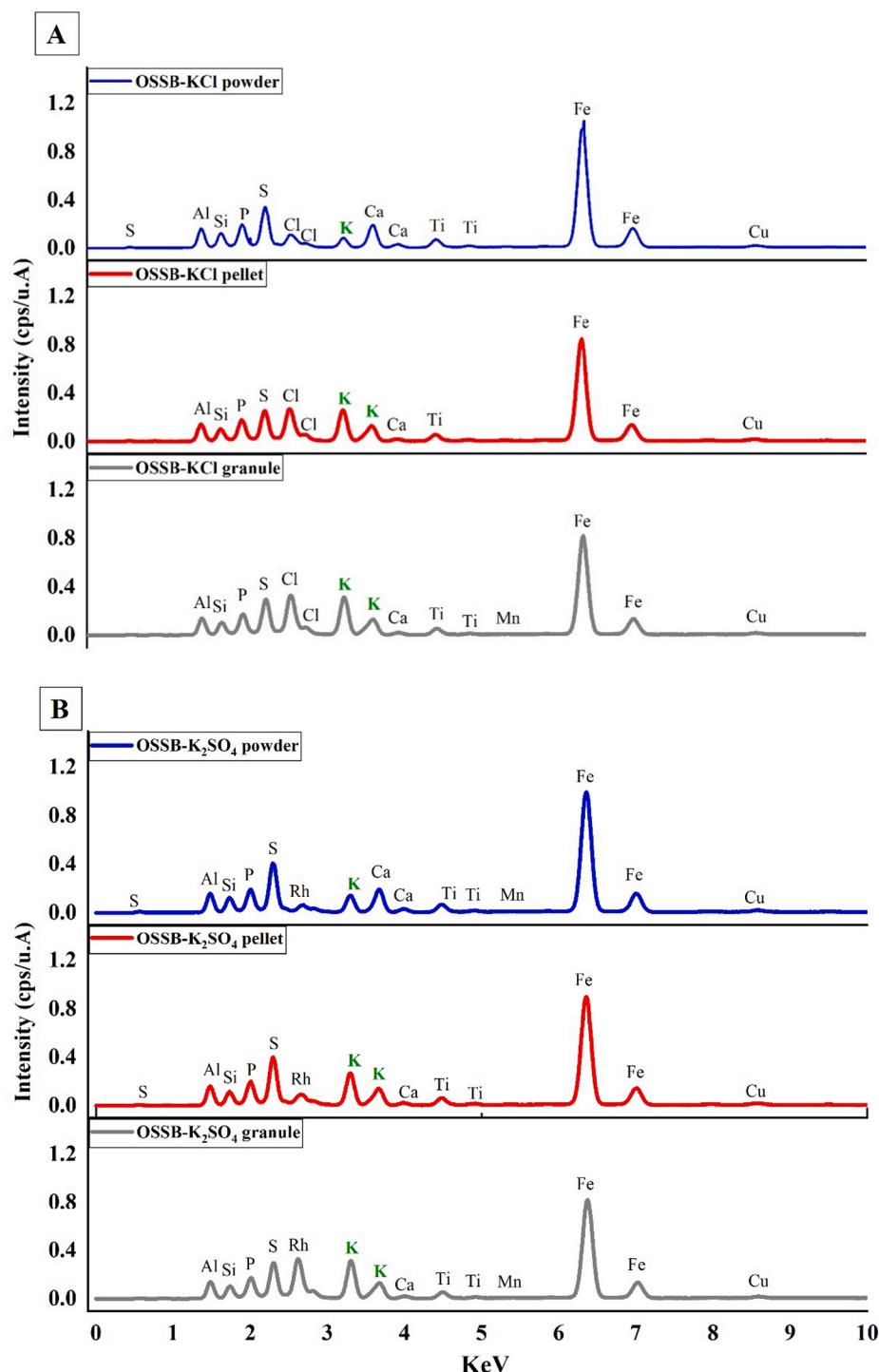


Fig. 1. Energy dispersive X-ray spectrometry (EDX) spectra of organomineral fertilizers enriched with KCl (A) and K_2SO_4 (B) in the form of granules, pellets and powder.

varying sizes and shapes to form a single granule of OSSB-KCl and OSSB- K_2SO_4 . Unlike granules, OSSB pellets showed a more compact and regular structure, with a smoother surface but with cracks (Fig. 3B and 3H).

In addition to the binder, compressing of raw materials in the pelletizer promotes a surface with less roughness and greater uniformity when compared to granules (Reza et al., 2012). Cracks on the surface of biochar pellets of different materials have also been reported in previous studies (Reza et al., 2014; Santos et al., 2015). The more compact structure with a smooth surface may be related to the decrease in pore volume of the pellets compared to other forms of organominerals.

Fig. 3C and 3I show the organomineral fertilizers in powder form (OSSB-KCl and OSSB- K_2SO_4 , respectively), which present a physical mixture of different particles with different sizes and shapes representing SSB and K sources. In general, K sources did not influence the shape of the granules, pellets and powders, since they were the smallest proportion in the organomineral mixture.

Fig. 3D, 3E, 3F, 3J, 3K and 3L with 3500x magnification show the surface roughness dominated by pores of varying sizes and well-distributed slits in the three different shapes of the OSSB-KCl and OSSB- K_2SO_4 . Also observed was the presence of particles of the minerals

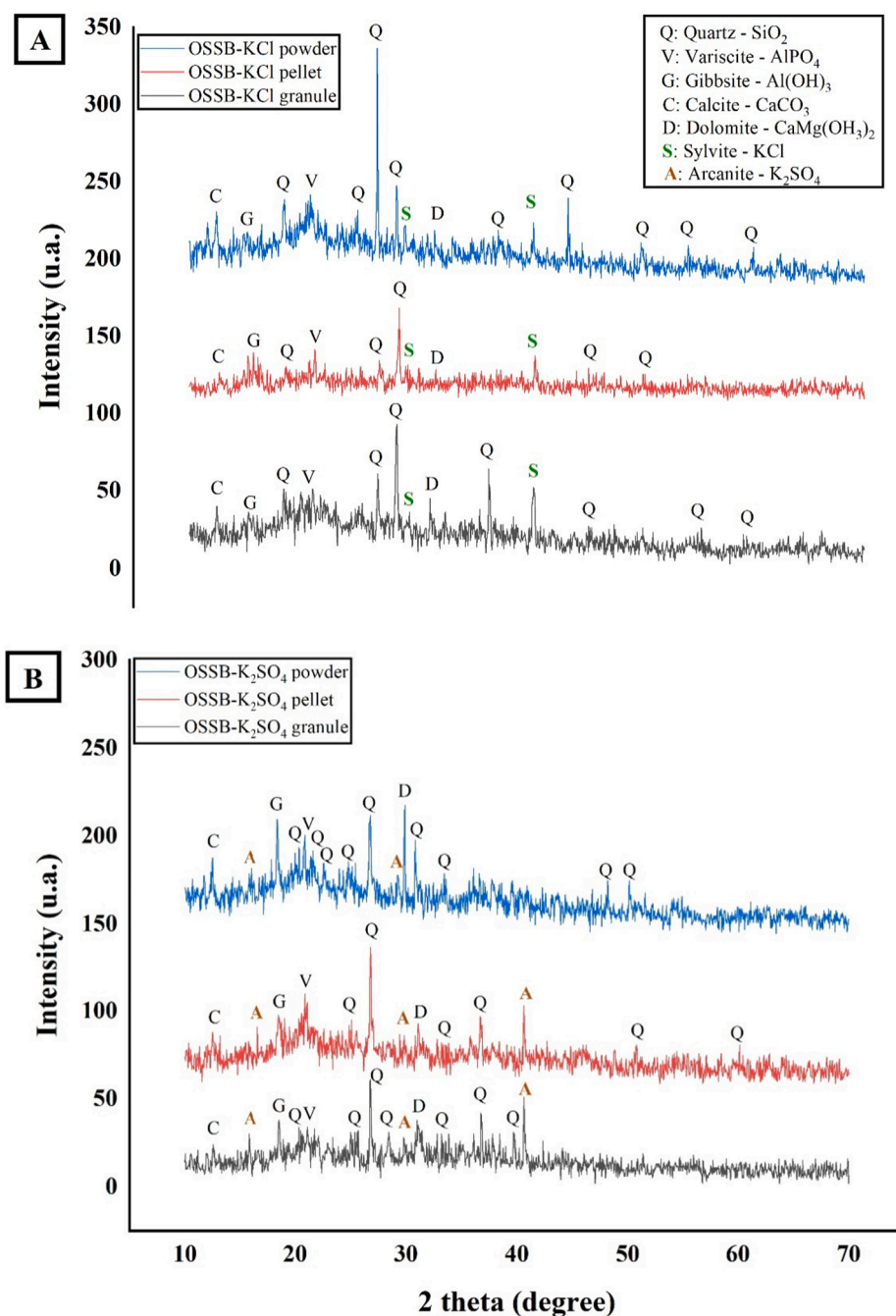


Fig. 2. X-ray diffraction (XRD) spectra of organomineral fertilizers enriched with KCl (A) and K_2SO_4 (B) in the form of granules, pellets and powder.

KCl (Fig. 3D, 3E and 3F) and K_2SO_4 (3 J, 3 K and 3L) on the surface of the SSB, and pores filled with minerals, indicating that the potassium fertilizer was adequately incorporated during the mixing of raw materials (Lin et al., 2013).

3.2.2. Surface area and pore volume

Nitrogen adsorption and desorption isotherm models described by Brunauer–Enmett–Teller (BET) for the different organomineral fertilizers are shown in Fig. 4. BET-analysis is widely used for surface area and porosity measurements. However, this method bears some limitations as diffusion problems in micropores (diameter $< \text{\AA} = 2 \text{ nm}$) can occur and the surface area might therefore be underestimated (Weber and Quicker, 2018). In the present study, the isotherms of all materials were Type IV(a) with Type H3 loop, according to the IUPAC

classification. This indicates that SSB and OSSBs predominantly present mesopores and macropores (Huang et al., 2017; Wang et al., 2016). The pyrolysis temperature governs the total pore volume (PV) and the surface area (SA) of pure SSBs (Figueiredo et al., 2018; Singh et al., 2020). At high pyrolysis temperatures SA and PV are usually higher than at low temperatures, i.e., 300°C (Singh et al., 2020). In the present study, SSB, produced at 300°C , had SA ($27.8 \text{ m}^2/\text{g}$) and PV ($0.102 \text{ cm}^3/\text{g}$) similar to or higher than values presented by other studies with SSB (Yuan et al., 2015; Figueiredo et al., 2018; Chagas et al., 2021; Figueiredo et al., 2021). In general, OSSB production reduced SA, PV and micropores volume (PMV). Regarding the PV, SSB presented 39% micropores and regardless of the K source, the OSSBs reduced the PV, presenting average values of 26, 27 and 23% micropores, in granules, pellets and powders, respectively. Among organomineral fertilizers, pellets showed the

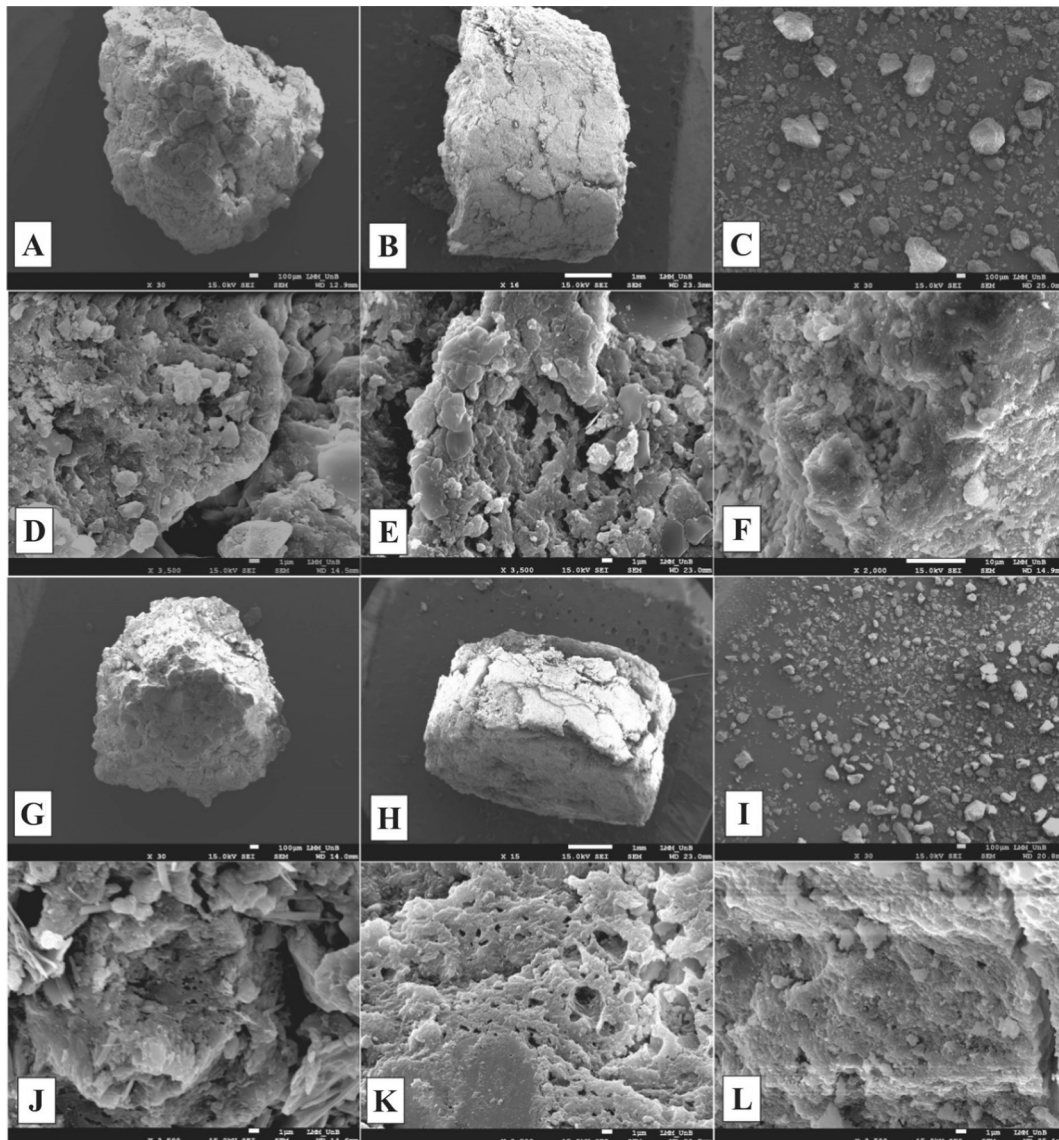


Fig. 3. Scanning electron microscopy images (SEM) of the OSSB granules, pellets and powders. A, B and C: OSSB-KCl in the form of granules (with 30x magnification), pellets (with 15x magnification) and powder (with 30x magnification), respectively; D, E and F: OSSB-KCl in the form of granules, pellets and powder, respectively, with 3500x magnification; G, H and I: OSSB-K₂SO₄ granules (with 30x magnification), pellets (with 15x magnification) and powder (with 30x magnification), respectively; J, K and L: OSSB-K₂SO₄ in the form of granules, pellets and powder, respectively, with 3500x magnification.

lowest SA, PV and PMV, confirming the effect of compaction promoted during pelletization, as observed in the SEM images (Fig. 3). In this sense, granulation showed higher values of SA, PV and PMV than the pellet, but lower than the product in a powder form.

Lower SA in organomineral fertilizers may also be related to the presence of mineral particles on the surface of the SSB and the filling of SSB pores with the K source after the enrichment process (Fig. 4). In addition, the SA value is generally related to the porosity of the material (Hsu et al., 2019), mainly with the micropore volume (Frazão et al., 2019). In the present work this relationship became clear because the material with the highest PMV was also that with the highest SA (SSB).

Micropores (<2 nm) contribute to SA and are considered essential for nutrient adsorption. On the other hand, mesopores can provide adequate shelters for microorganisms, increasing their survival and spread, and macropores can increase water infiltration and soil aeration (Gao et al., 2016). The greater the pore volume the easier it is for water and plant roots to penetrate, facilitating contact with the material particles and favoring the release and absorption of nutrients. Fertilizers with higher porosity tend to have a higher rate of nutrient release when

compared to fertilizers with thicker and smoother layers (Hermawan and Adipati, 2018).

3.2.3. Apparent density (AD) and particle density (PD)

The K source did not affect the AD and PD of organomineral fertilizers. On the other hand, the DA was affected by the physical form of the fertilizer (Table 4). The powdered OSSB fertilizers showed a higher AD, and the granules presented the lowest values. The pellet showed an intermediate AD value. The higher AD of the organomineral fertilizer in a powder form is related to the predominance of small particles (<0.500 mm). As a consequence, a larger mass of powdered fertilizer can be stored per unit volume.

There was no difference between the forms of enriched organomineral fertilizers in terms of PD values. Contrary to our results, pellets usually have a higher PD than granules due to the pelletizing process. Compression reduces gaps and voids between the particles of the material (Reza et al., 2012), requiring a larger amount of biomass to form a pellet. In the granulation process the material is not subjected to compression, presenting a more porous structure in the middle of the

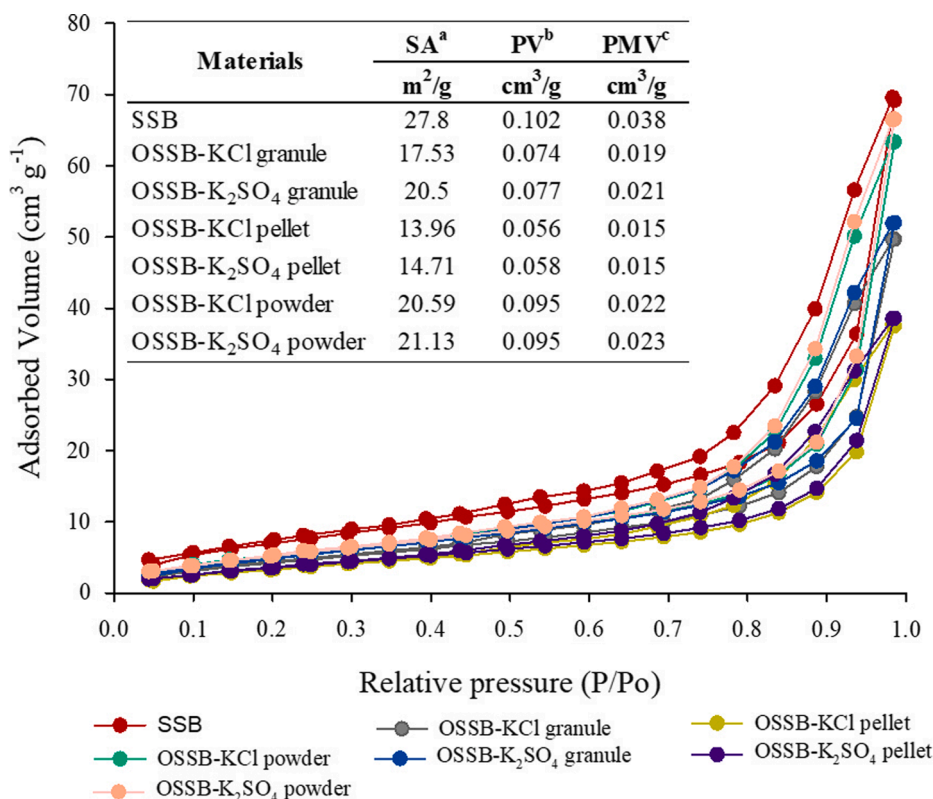


Fig. 4. Nitrogen adsorption/desorption isotherms of SSB and organomineral fertilizers enriched with KCl (OSSB-KCl) and K₂SO₄ (OSSB-K₂SO₄) in three physical forms: granules, pellets and powder. ^a: surface area; ^b: total pore volume; ^c: micropores volume.

Table 4

Apparent density (AD) and particle density (PD) of K-enriched organomineral fertilizers.

Source	AD (g cm ⁻³) ¹		PD (g cm ⁻³) ²	
OSSB-KCl	0.56a	a	1.0	a
OSSB-K ₂ SO ₄	0.55a	a	1.0	a
Form				
Granule	0.45	c	0.9	a
Pellet	0.50	b	1.0	a
Powder	0.74	a	–	

Means followed by the same letter are not statistically different according to the Tukey test ($P < 0.05$). Reference values (range) of various organomineral fertilizers reported in literature ¹: AD = 0.52 – 1.0 g cm⁻³ (Antille et al., 2013; Gurgel et al., 2015; Herwman et al., 2018); ²: PD = 1.3 – 1.8 g cm⁻³ (Paré et al., 2010; Antille et al., 2013).

granule when compared to the pellet structure (Vincevica-Gaile et al., 2019). According to Hu et al. (2016), a higher PD indicates a lower percentage of empty spaces and gaps within the material. In the present study, the PD values of enriched OSSBs, pelletized and granulated, are within the PD range already reported in other studies with biochars, with values varying between 0.6 and 1.7 g cm⁻³ for pellets and granules, respectively (Hu et al., 2016; Reza et al., 2014; Vincevica-Gaile et al., 2019).

Apparent density, PD and granulometry are important physical characteristics of fertilizers that influence the storage and application of the product. The development of new fertilizers requires the determination of physical properties of the materials, because they affect storage, spreading, behavior in the soil and agronomic efficiency (Antille et al., 2013). Thus, organomineral fertilizers in the form of granules and pellets need a larger storage space to store the same mass of powdered organomineral fertilizer.

However, in its powder form, biochar can have very fine particles

(1–600 μm) (Bowden-Green and Briens, 2016) that can be transported by the air. This causes health risks to people exposed to the product, such as respiratory irritation and pulmonary damage, thus making its application in the field unviable. Additionally, its low density promotes the accumulation of biochar in the upper soil layers, hindering its interaction in the soil profile (Vincevica-Gaile et al., 2019). Granulation and pelletization of SSB enriched with K are therefore means of minimizing the risks of dust and respiratory problems caused by the application of powdered biochars. Additionally, granules and pellets are easier-to-apply materials.

4. Conclusions

The enrichment of SSB with soluble sources of potassium (K) produces organomineral fertilizers with great potential for agriculture. The K source influenced both the chemical and mineralogical composition of the OSSBs due to the proportions of raw materials used. The morphology and physical characteristics of OSSBs were more influenced by the shape of the fertilizer (powder, pellet or granule) than by the source of K (KCl or K₂SO₄). Future studies are needed to evaluate the release dynamics of K from OSSBs in the soil and the K uptake by crops. In addition, the scaling-up process and economic analysis need to be better understood.

Declaration of Competing Interest

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

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.wasman.2021.08.027>.

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