Vol.65: e22210592, 2022
https://doi.org/10.1590/1678-4324-2022210592
ISSN 1678-4324 Online Edition

Article - Agriculture, Agribusiness and Biotechnology

Pyrolysis of Sewage Sludge: Physical, Chemical, Morphological and Mineralogical Transformations

Jóisman Fachini[1]
https://orcid.org/ 0000-0002-2780-7715

Cícero Célio de Figueiredo[1]*
http://orcid.org/0000-0002-7496-0261

[1]University of Brasília, Faculty of Agronomy and Veterinary Medicine, Brasília, DF, Brazil.

Editor-in-Chief: Alexandre Rasi Aoki
Associate Editor: Ana Cláudia Barana

Received: 07-Sep-2021; Accepted: 08-Dec-2021.

*Correspondence: cicerocf@unb.br; Tel.: +55-61-31077465 (C.C.F.)

HIGHLIGHTS

- Biochar from sewage sludge (SS) was produced and characterized.
- Pyrolysis increased organic and total carbon.
- Pyrolysis increased micro and macronutrients concentration with exception of K.
- Biochar preserved the mineralogical characteristics of the raw material.
- Pyrolysis is an excellent alternative to transform SS into organic fertilizer.

Abstract: The sewage sludge (SS) use in agriculture has been limited by the Brazilian legislation to a few situations, mainly as a precautionary measure due to inorganic pollutants and pathogens. Thus, a large amount of SS has been accumulated in landfills, with no prospect of use, generating great concern for governments and society. Thermal treatment via pyrolysis has stood out as an option for SS recycling, transforming it into a carbon-rich product known as SS biochar (SSB). Biochar from SS showed good potential to be used for agricultural and environmental purposes. The present study aimed to evaluate the influence of pyrolysis at 300°C on the physical, chemical, morphological and mineralogical characteristics of SSB. In general, pyrolysis increased total carbon, total nitrogen, macro and micronutrient contents, except potassium. Pyrolysis also increased heavy metals (HMs) concentration in SSB. However, HMs values remained below the maximum limits allowed according to the legislation on SS agricultural use. X-ray analysis showed that both SS and SSB present silica (SiO_2) as the main mineral. Pyrolysis also increased the SS surface area (SA) and porosity. In general, results of the present study prove showed that pyrolysis is a technological alternative to enable SS use as a sustainable input in agriculture.

Keywords: biochar; thermal treatment; elemental composition.

INTRODUCTION

Compared to other biomasses, sewage sludge (SS) is considered a residue rich in nutrients and organic matter (OM) [1]. Sewage sludge can be used in agriculture as a soil amendment, among other functions [2]. Despite this potential, according to the Brazilian regulation, CONAMA Resolution 498 [3], SS should be applied in a few situations, mainly as a precautionary measure due to the presence of inorganic pollutants and pathogens. The most common sources of heavy metals (HM) in SS are domestic and industrial wastewaters and corrosion of sewerage systems, as well as surface runoff from urbanized areas or roads. Other sources of HMs are pharmaceuticals, body care and cleaning products [4].

Consequently, a large amount of SS is accumulated in landfills, with no prospect of use, generating great concern for governments and society. Therefore, technological alternatives must be sought so that the agricultural use of SS is not neglected. Pyrolysis is the thermochemical conversion of biomass in the absence or under limited oxygen. The solid product of pyrolysis, rich in carbon, is called biochar and can be used as a soil amendment. Pyrolysis has stood out as an option for SS recycling, transforming it into a material free of pathogenic organisms, rich in nutrients such as nitrogen (N), phosphorus (P), calcium (Ca) and zinc (Zn) [1], called SS biochar (SSB).

In general, the nutrient concentration in biochars varies according to the raw material and pyrolysis conditions [5, 6]. Among feedstocks used for producing biochar, SS is considered a nutrient-rich material. In addition, recent research has shown that as a soil amendment SSB can provide nutrients and increase the use efficiency of several plant nutrients, resulting in high crop yields [5, 7, 8].

Depending on pyrolysis conditions, SSB can have up to 6% P in its final composition [9]. Faced with an uncertain future of world reserves of phosphate fertilizers, P recovered from various residues, such as SS, is a partial solution to this problem [10]. In a study by Yuan and coauthors [5] with SSB produced at different pyrolysis temperatures, the authors demonstrate that between 92% to 98% of SS P remains in the SSB.

As demonstrated earlier, SSB can be used for agricultural and environmental purposes. However, due to the great variety of characteristics among sludges obtained from different origins and types of treatments, there is still a lack of studies involving SSB characterization via a wide range of analytical techniques. It was hypothesized that pyrolysis alters the chemical, physical, morphological and mineralogical characteristics of SS. Therefore, the objective of this study was to evaluate the effect of pyrolysis on the transformations of SS, predominantly domestic, through chemical, physical, morphological and mineralogical characteristics.

MATERIAL AND METHODS

Preparation of sewage sludge biochar

The SSB was produced from SS samples collected at the Melchior wastewater treatment plant (WWTP), belonging to the Environmental Sanitation Company of the Federal District, Brasília, DF, Brazil. This WWTP utilizes the tertiary treatment system, in which the sewage decomposition is carried out in an anaerobic up-flow reactor (RAFA). In this 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 biochar preparation, SS samples were air-dried (to approximately 10% moisture content), passed through a 4 mm sieve and then submitted to pyrolysis at 300°C. This temperature was chosen based on our previous study [9] in which, considering all variables together, the biochar produced at 300 °C showed the greatest nutrients availability. Pyrolysis was performed in a muffle furnace (Linn Elektro Therm, Eschenfelden, Germany) at a mean temperature increase rate of 2.5°C min^{-1} and residence time of 05h00. The furnace was equipped with a mechanism to prevent oxygen flow (via forced draft fan, helping gas and oil vapors exit the furnace). Depending on the purpose, a shorter residence time can be adopted in future works.

Physical-chemical characterization of sewage sludge and biochar

Proximate analysis

Both SS and SSB samples were powdered and passed through a 0.250-mm mesh sieve and submitted to proximate analysis in order to determine moisture, volatile matter (VM), ash and fixed C (FC). Moisture, VM and ash contents were determined by heating the samples in a muffle furnace (Linn-Elektro Therm, model KK 260 SO 4060). Finally, FC was obtained by the difference between 100 and the sum of moisture, VM and ash in %.

Elemental analysis

Carbon, N and H were determined using an elemental analyzer (Euro EA3000 Elemental Analyser, Milano, Italy) equipped with a thermal conductivity detector. Samples (approximately 1.0 mg) were placed in auto-injector for sample run.

pH, nutrients and heavy metals (HMs)

Determinations of pH, nutrient and MPs contents were carried out according to the official analytical methods for fertilizers and correctives [11]. After drying, grinding and sieving through a 0.50 mm mesh sieve, samples were subjected to determination of pH, macronutrients and heavy metals contents. The pH was determined in a 0.01 M $CaCl_2$ solution, using a 1:5 (w/v) material:solution ratio suspension. Samples of SS and SSB were subjected to acid digestion with concentrated HCl/HNO_3. Macronutrient (Ca, Mg and S), micronutrients and HVs contents, were analyzed by ICP-OES (ICPE-9000, Shimadzu, Japan). After nitroperchloric extraction, the concentration of P was determined using the colorimetric method of molybdovanadophosphoric acid. The P concentration was estimated in a spectrophotometer at 400 nm (Automatic Digital Spectrophotometer SP 22, China).

Organic carbon (OC) and humic substances (HS)

The organic carbon (OC) content was determined by the volumetric method of potassium dichromate [12]. The determination of humic substances (HS) was performed according to the differential solubility technique [13]. Carbon levels of fulvic acid (FA), humic acid (HA) and humin (HU) were estimated by dichromatometry.

Adsorption/desorption isotherms, superficial area and pore volume

Surface area and pore volumes were determined by N_2 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. The standard BET procedure requires the measurement of at least five points in the appropriate pressure range on the N_2 adsorption isotherm at the normal boiling point of liquid N (-196.2°C).

Scanning electron microscope images (SEM)

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

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

The X-ray diffraction (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°. Samples were also submitted to energy dispersive X-ray spectrometry (EDX) analysis. EDX patterns were obtained using an EDX 720HS (Shimadzu) spectrometer. For both analysis (XRD and EDX) whole samples were used.

Statistical analysis

For the macronutrients and micronutrients, elemental composition, proximate analysis properties, surface area and pore volume, comparisons between the SSB and the SS were performed considering the relative enrichment factor (RE), where $C_{biochar}$ is the content of property in biochar and C_{feed} is the content of property in the SS, according to the Equation 1 used by Yuan and coauthors [14]:

$$RE = \frac{Cbiochar}{Cfeed} \quad (1)$$

RESULTS AND DISCUSSION

Physical and chemical characteristics

The results obtained by physical-chemical analysis indicate a clear influence of pyrolysis on the properties of SSB. The pyrolysis process reduced moisture (RE = 0.81) and volatile matter (RE = 0.85), and increased ash (RE = 1.18) and FC (RE = 4.2) levels in samples (Table 1). The increase in ash content is expected, since up to 600°C most of the mineral material is preserved and volatile compounds are lost, resulting in a higher ash concentration [15]. The pH value was not altered by pyrolysis and it was close to neutrality (6.5), similar to results previously reported for biochars obtained at low temperatures (300ºC) [7, 8]. Typically, increases in pH are observed at higher pyrolysis temperatures (> 400°C). SSB had a FC content 4.2 times higher than SS, and a smaller increment was verified for TC, ranging from 25.1% in SS to 27.1% after pyrolysis. These results demonstrate that pyrolysis promotes a greater accumulation of more recalcitrant forms of C, due to the reorganization of aliphatic chains into condensed C forms [16].

Table 1. Physical and chemical characteristics and relative enrichment factor (RE) from sewage sludge (SS) and biochar (SSB).

Property[a]	**SS**	**SSB**	**RE**[b]
pH ($CaCl_2$)	6.4±0.05	6.5±0.02	1.02
Moisture (%)	10.4±0.11	8.4±0.03	0.81
Volatile matter (%)	55.7±0.32	47.2±0.49	0.85
Ash (%)	32.4±0.17	38.1±0.18	1.18
FC (%)	1.5±0.19	6.3±0.64	4.20
OC (%)	18.3±0.11	18.3±1.06	1.08
H (%)	4.1±0.17	2.7±0.04	0.65
TC (%)	25.1±0.17	27.1±0.08	1.10
TN (%)	3.9±0.17	4.3±0.13	1.17
C/N	6.4±0.11	6.3±0.17	0.80
Total P_2O_5 (%)	4.7±0.07	5.5±0.08	1.15
Total K_2O (%)	0.05±0.01	0.04±0.01	1.10
Ca (g kg $^{-1}$)	6.0±0.03	6.9±0.04	1.25
Mg (g kg $^{-1}$)	1.40±0.2	1.54±0.01	1.14
S (g kg $^{-1}$)	1.30±0.4	1.62±0.01	1.18
Fe (g kg $^{-1}$)	17.5±1.06	20.0±2.1	1.13
B (mg kg $^{-1}$)	26.4±3.0	31.2±1.1	1.18
Mn (mg kg $^{-1}$)	88.6±4.2	100.0±11.3	1.14
Zn (mg kg $^{-1}$)	414.2±19.1	453.9±2.1	1.23
Cu (mg kg $^{-1}$)	88.1±5.5	100.0±2.3	1.25
Co (mg kg $^{-1}$)	9.7±0.6	11.9±1.9	1.22
Mo (mg kg $^{-1}$)	33.9±0.1	42.4±2.5	1.25
Cd (mg kg $^{-1}$)	18.1±0.7	19.3±3.5	1.07
Cr (mg kg $^{-1}$)	47.3±2.7	53.0±0.1	1.12
Ni (mg kg $^{-1}$)	14.4±1.3	28.4±0.6	1.96
Pb (mg kg $^{-1}$)	414.2±19.1	148.5±0.7	0.36
FA (g kg^{-1})	35.0±0.85	33.7±0.82	1.00
HA (g kg^{-1})	14.9±0.55	9.3±1.60	0.62
HU (g kg^{-1})	179.1±0.58	229.4±8.08	1.28
SA (m^2/g^{-1})	21.9	27.8	1.02
PV (cm^3/g^{-1})	0.096	0.102	1.10

[a]: average values ± standard deviation (n = 3); [b]: relative enrichment factor; FC = fixed carbon; OC = organic carbon; TC = total carbon; TN = total nitrogen. FA: fulvic acid; HA: humic acid; HU: humin; SA: specific surface area; PV: pore volume.

The NT content increased from 3.9% to 4.3% after pyrolysis (RE = 1.17). This increase indicates the presence of compounds in SSB with structures that are not easily decomposed up to 300 °C [9]. Thus, the higher NT concentration in SSB can be explained by the volatilization losses of other elements and water. As expected, SS showed low K concentration, being little altered by pyrolysis. Consequently, SSB was poor in K, as reported previously [17]. This is the main limitation when using SSB as a fertilizer. In this case, further studies should search alternatives to provide K sources together with SSB. Enriching SSB with K and co-pyrolysis of SS with K-rich raw materials [6] or produce of K-enriched organomineral fertilizer from SSB [18] are some promising technologies.

Except for K, SS pyrolysis enriched macro and micronutrients levels. The total P_2O_5 concentration in SSB was 5.5%. This value was14% higher than in SS. This increase usually occurs up to 700 °C, at which P losses start due to volatilization [14]. Compared with biochar from multiple feedstocks [19] and with other types of soil amendments [20], SSB has higher P levels, with great potential for use as a P fertilizer. Increases of Ca, Mg, S and micronutrients levels have also been reported in previous studies with SSB at 300ºC [8, 17, 21].

Pyrolysis also increased HMs levels (Table 1). Similar results also indicated higher HM content in SSB than in SS [21]. During the SS pyrolysis process, there may be an increase in the concentration of non-volatile elements in the temperature range used, leading to higher HM contents [22]. Therefore, because HMs have a higher boiling point than the pyrolysis temperature employed, they are concentrated in the final biochar [21]. Pyrolysis also increases the thermostability of HMs, where examples may include the various forms in which HMs can exist in SS, salts and hydroxides are generally converted to oxides or sulphides, which are more stable at elevated temperatures [22]. Despite this, the HMs concentration was below the maximum limits acceptable by Brazilian legislation [3] and the European Union [23] for SS and the maximum limits allowed by the International Biochar Initiative for biochar [24]. The origin of the SS produced in Brasilia, Brazil, is predominately domestic with low HM concentration. Therefore, biochar produced from SS generated in this city has a low risk of soil contamination, as demonstrated in our previous works, including short-term [25] and long-term assessments [21].

The pyrolysis process reduced the TC and FA and HA contents and increased HU concentration. Lower levels of FA and HA may result from thermal degradation of organic compounds during the pyrolysis process [26], thus increasing the C content in HU, which is the most recalcitrant fraction of OM. In addition, biochars contain highly aromatic polycondensed compounds very similar to the HU fraction [9], which may increase this fraction compared to SS.

X-ray Spectra by energy dispersive spectrometry

In the X-ray spectra it is possible to confirm the low presence of K in both SS (Figure 1A) and SSB (Figure 1B). Contrarily, the spectra of both materials confirmed the presence of P and other nutrients such as S, Ca, manganese (Mn), iron (Fe) and aluminum (Al). Small increases in intensity were observed after pyrolysis, 0.028 cps/uA and 0.1656 cps/uA for K and P, respectively. These results demonstrate that pyrolysis at 300°C promoted little change in the composition of these elements. Previous studies reported that the most significant changes in these SSB elements, compared to SS, were only found in biochars obtained at higher temperatures [9, 22].

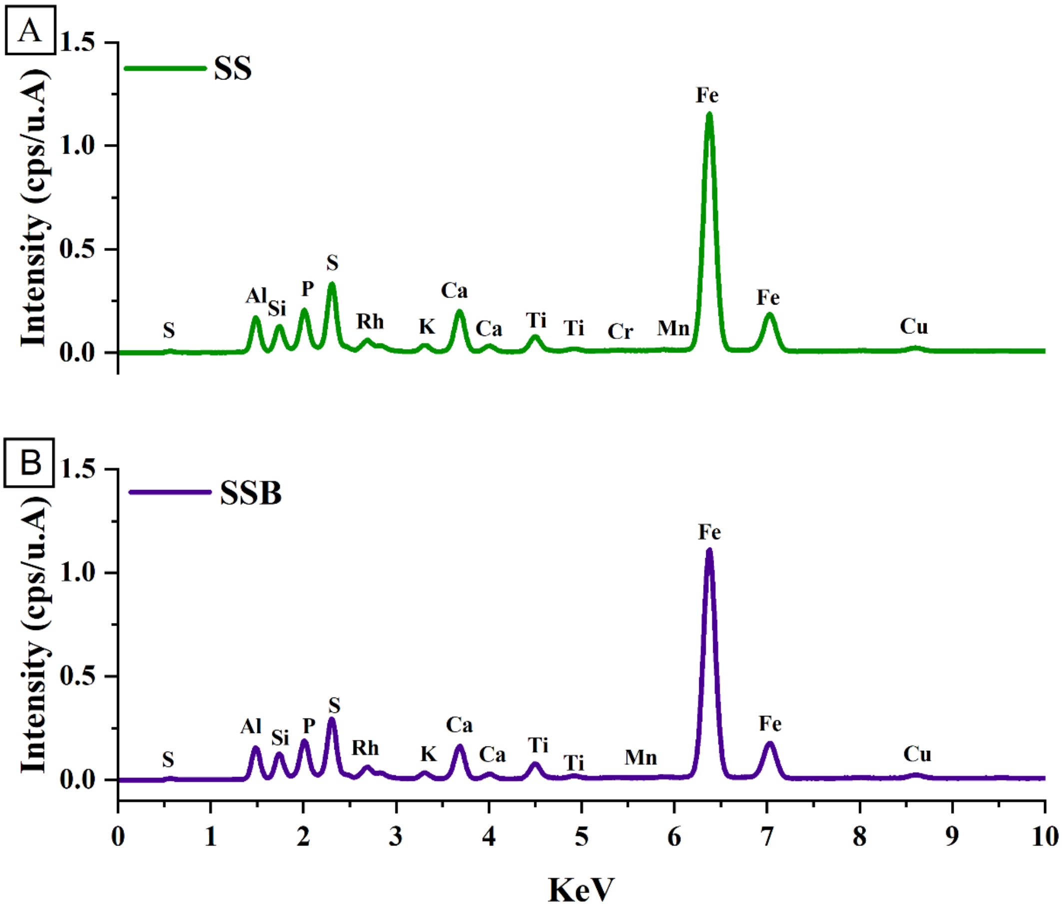

Figure 1. Energy dispersive X-ray spectrometry (EDX) spectra of sewage sludge (SS) and biochar (SSB).

X-ray diffraction (XRD) spectra

The X-ray diffraction spectra (XRD) (Figure 2) demonstrated that quartz (SiO_2) was the main mineralogical component of SS (Figure 2A) and SSB (Figure 2B), with peaks close to 21°, 26º, 31°, 36°, 41°, 55°, 60°, 64° and 68° for SS and 21°, 26°, 45° and 68° for SSB. Usually, quartz is the most abundant mineral in SS and SSB samples, mainly due to clay and sand that remain in the sludge after the sewage treatment [27, 28]. Less intense peaks were also observed, in SS and SSB, at 18°, 22°, 25°, 27° and 29°, which show, respectively, the presence of gibbsite [$Al(OH)_3$], variscite ($AlPO_4$), dolomite [$CaMg(CO_3)_2$], calcite ($CaCO_3$) and albite ($NaAlSi_3O_8$) [28]. In SSB, the increase in peaks during the range of 2Θ = 20 to 30° indicates a C-rich structure with graphite-like amorphous structures stacked in layers [29]. In general, after the pyrolysis, SSB maintained the mineralogical characteristics of SS, probably due to the low temperature used. The only difference found was the presence of more intense peaks of quartz in SSB compared to SS. The XRD spectra reinforce the results obtained in chemical analyzes (Table 1) and the EDX spectra (Figure 1B) that demonstrated the presence of silicon (Si), Fe, Al, P, Ca and Mg in SSB.

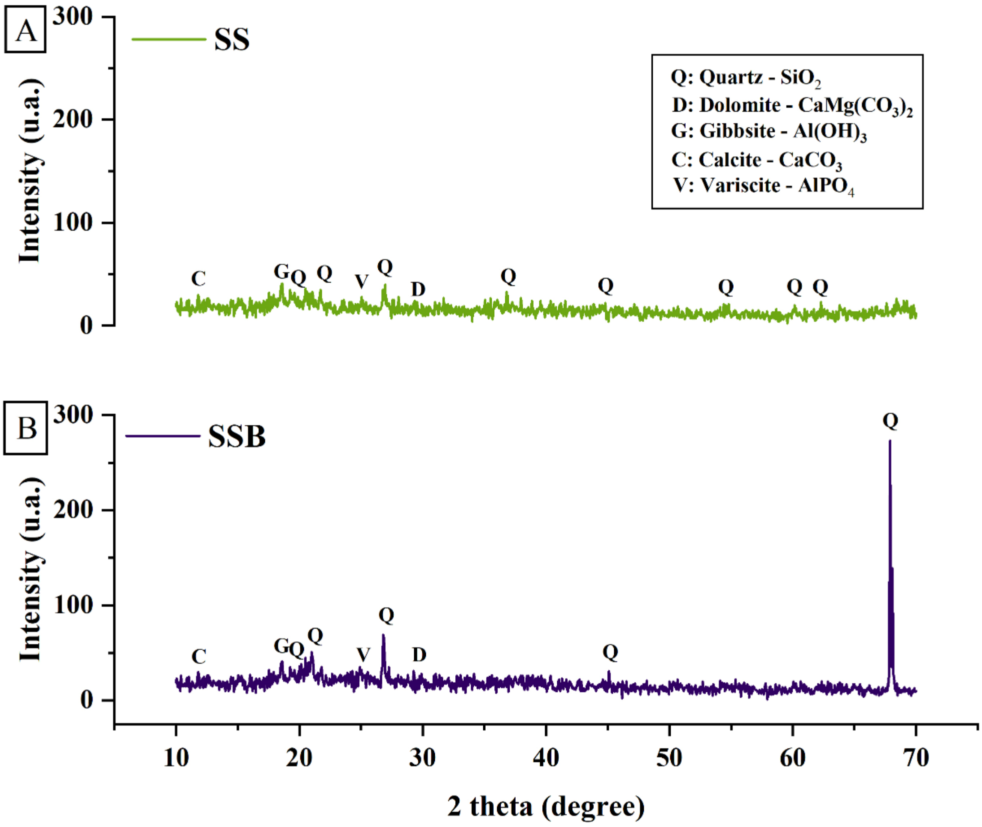

Figure 2. X-ray diffraction (XRD) spectra of SS (A) and SSB (B).

Scanning electron microscope images

SEM images of the SS and SSB samples are shown in Figure 3. The SSB sample has a darker color with a typical charcoal appearance (Figure 3D) compared to the SS images (Figure 3A). Figures 3B and 3E show the irregular shape of the SS and SSB samples, in addition to showing a greater presence of impurities on the SS surface and the presence of very small aggregates and stabilized particles on the SSB surface. The greater presence of pores in SSB (Figure 3F) than in SS (Figure 3C) can also be observed, contributing to a greater SA in biochars [30].

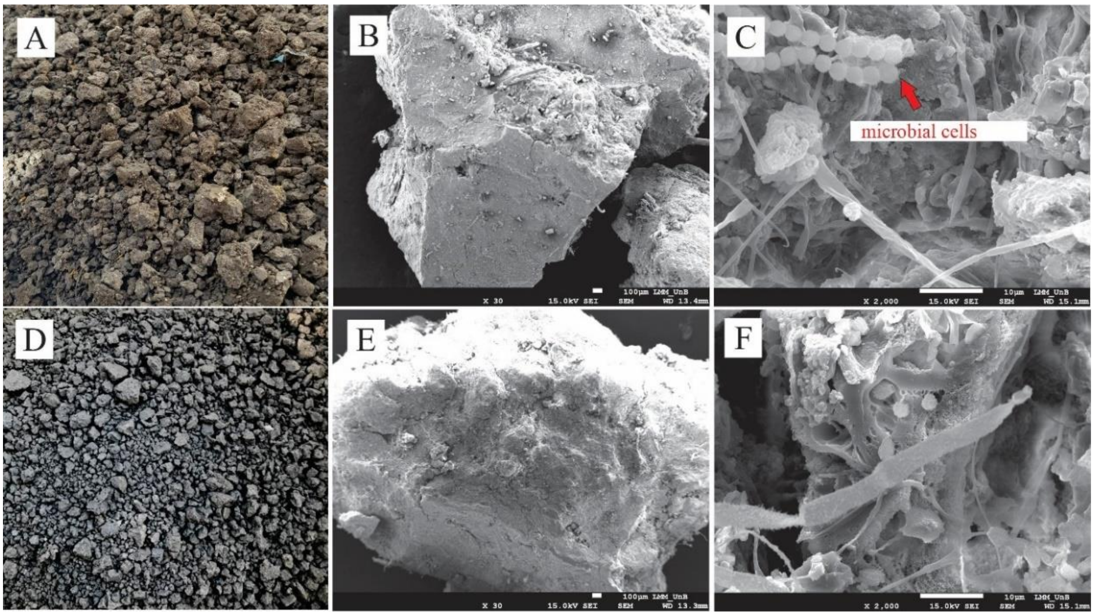

Figure 3. Scanning electron microscopy images of the SS and SSB surfaces. A: crushed SS; B: SS surface with a 30x magnification; C: SS surface with 2000x magnification. D: SSB; E: SSB with a 30x magnification. F: SS surface with 2000x magnification.

The presence of microbial cells in abundance in the SS sample should also be noted (Figure 3C), possibly composed of pathogenic microorganisms that persist even after the SS has dried. Pyrolysis temperatures ≥300°C can inactivate helminths and thermotolerant coliforms, as demonstrated in our previous study [25].

Surface area and pore volume

Nitrogen adsorption and desorption isotherm models described by Brunauer–Enmett–Teller (BET) Model for the SS and SSB are shown in Figure 4. BET-analysis is widely used for SA and porosity measurements.

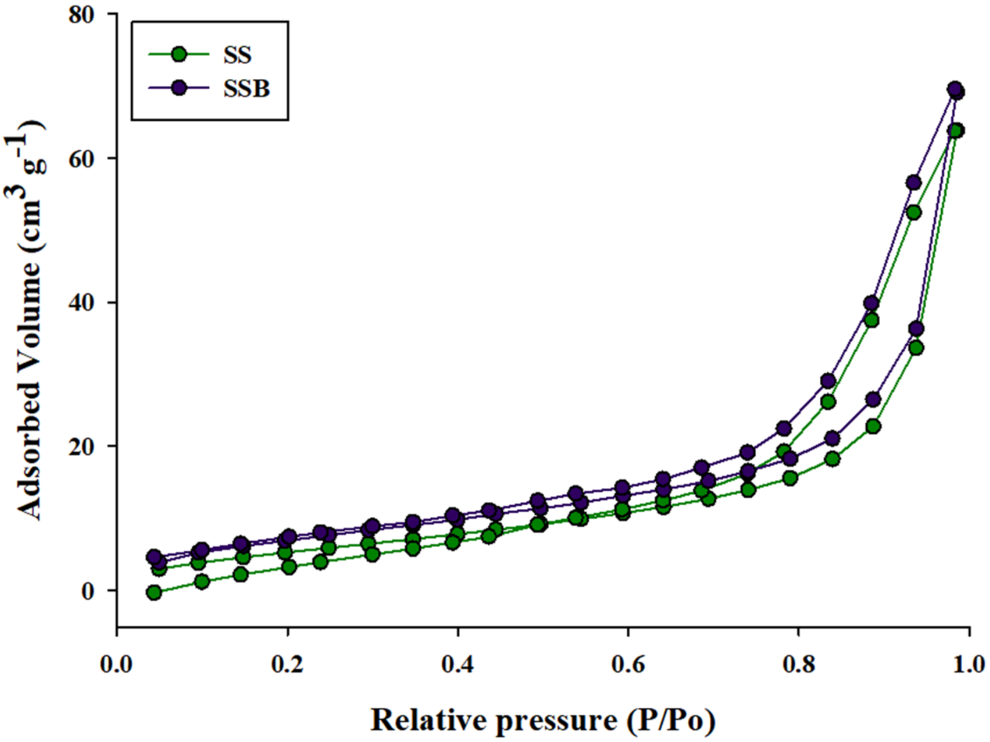

Figure 4. Nitrogen adsorption/desorption isotherms of SS and SSB.

In the present study, the isotherms of both materials were Type IV(a) with Type H3 loop, according to the IUPAC classification. This indicates that SS and SSB predominantly present mesopores and macropores [31, 32, 33]. Larger total pore volume (PV) and SA are desirable characteristics since they promote greater contact between the biochar and soil colloids and water, favoring the release of plant nutrients [34]. In addition, larger pores can serve as an adequate shelter for microorganisms, increasing their survival and spread, in addition to improving water retention and soil aeration [35].

As shown in Table 1, the pyrolysis increased SA and PV. The increase was 27 and 6.25% for SA and PV respectively. The increase in PV is due to the increase in SA after a pyrolysis [25]. In the present study, SSB, produced at 300 °C, had SA (27.8 m^2/g) and PV (0.102 cm^3/g) similar to or higher than values presented by other studies with SSB [9,17, 22, 36]. In addition, the SA value is generally related to the porosity of the material, mainly with the micropore volume [29]. In the present work, this relationship became clear because the material with the highest PV was also that with the highest SA (SSB).

CONCLUSION

Sewage sludge pyrolysis increased the TC, TN and macro and micronutrient contents in SSB. The biochar showed a higher concentration of heavy metals. Despite this, the MP contents were below the maximum limits allowed for SS agricultural use. Also, SS pyrolysis at 300°C was insufficient to increase the concentration of K in SSB, due to the low presence of this element in the raw material. Biochar preserved the mineralogical characteristics of the raw material, whose main mineral was quartz. The pyrolysis process also increased the SA and PV, which are desirable characteristics for a sustainable-based fertilizer. It is possible to conclude that pyrolysis is an excellent alternative to transform SS into organic fertilizer and thus contribute to the recycling of SS in agriculture.

Funding: This research received no external funding.
Acknowledgments: The second author thanks the National Council for Scientific and Technological Development (CNPq) for the fellowship of scientific productivity.
Conflicts of Interest: The authors declare no conflict of interest.

REFERENCES

1. Paz-Ferreiro J, Nieto A, Méndez A, Askeland M, Gascó G. Biochar from biosolids pyrolysis: a review. Int. J. Environ. Res. Public Health. 2018;5(15):e956. https://doi.org/10.3390/ijerph15050956.
2. Kirchmann H, Börjesson G, Kätterer T, Cohen Y. From agricultural use of sewage sludge to nutrient extraction: A soil science outlook. Ambio. 2021;46:143-54. https://doi.org/10.1007/s13280-016-0816-3.
3. Brazil. National Council for the Environment. Resolution nº 498 of August 19, 2020. Official Gazette of the Union, Executive Branch, Brasília – DF, August 21, 2020.
4. Duan B, Zhang W, Zheng H, Wu C, Zhang Q, Bu Y. Disposal situation of sewage sludge from municipal wastewater treatment plants (WWTPS) and assessment of the ecological risk of heavy metals for its land use in Shanxi, China. Int. J. Environ. Res. Public Health 2018;14:823.
5. Yuan H, Lu T, Wang Y, Chen Y, Lei T. Sewage sludge biochar: Nutrient composition and its effect on the leaching of soil nutrients. Geoderma. 2016;267:17-23. https://doi.org/10.1016/j.geoderma.2015.12.020.
6. Najafi-Ghiri M, Boostani HR, Hardie AG. Investigation of biochars application on potassium forms and dynamics in a calcareous soil under different moisture conditions. Arch. Agron. Soil Sci. 2020;66:e225163308. https://doi.org/10.1080/03650340.2020.1834083.
7. Faria WM, Figueiredo CC, Coser TR, do Vale AT, Schneider BG. Is sewage biochar capable of replacing inorganic fertilizers for corn production? Evidence from a two – year field experiment. Arch. Agron. Soil Sci. 2018;64:505-19. https://doi.org/10.1080/03650340.2017.1360488.
8. Fachini J, Coser TR, de Araujo, AS, do Vale AT, Jindo K, Figueiredo CC. One year residual effect of sewage sludge biochar as a soil amendment for Maize in a Brazilian Oxisol. Sustainability. 2021;13:e2226. https://doi.org/10.3390/su13042226.
9. Figueiredo CC, Lopes HM, Coser TR, Vale AT, Busato JG, Aguiar NO, et al. Influence of pyrolysis temperature on chemical and physical properties of biochar from sewage sludge. Arch. Agron. Soil Sci. 2018;64:881-9. https://doi.org/10.1080/03650340.2017.1407870.
10. Kleemann R, Chenoweth J, Clift, R, Morse S, Pearce P, Saroj D. Comparison of phosphorus recovery from incinerated sewage sludge ash (ISSA) and pyrolyzed sewage sludge char (PSSC). Waste Manage. 2017;60:201-10. https://doi.org/10.1016/j.wasman.2016.10.055.
11. Brazil. Ministry of Agriculture, Livestock and Food Supply, 2017. The Official Methods of Analysis of Fertilizers and Correctives. Agricultural Defense Secretariat. Brasília: MAPA, p. 240.
12. Walkley A, Black IA. An examination of the Degtjareff method for determining soil organic matter and a proposed modification of the chromic acid titration method. Soil Sci. 1934;37:29-38, https://doi.org/10.1097/00010694-193401000-00003.
13. Swift RS. Method for extraction of IHSS soil fulvic and humic acids. In: Sparks DL, Page AL, Helmke P A , Loeppert R H , Soltanpour P N , Tabatabai MA, Johnston CT, Summer ME. Methods of soil analysis: Chemical methods. Soil Sci. Soc. Am. J. 1996;3:1018-20.
14. Yuan H, Lu T, Zhao D, Huang H, Noriyuki K, Chen Y. Influence of temperature on product distribution and biochar properties by municipal sludge pyrolysis. J. Mater. Cycles Waste Manage. 2013;15:357–61. https://doi.org/10.1007/s10163-013-0126-9.
15. Adhikari A, Gascó G, Méndez A, Surapaneni A, Jegatheesan V, Shah K, et al. 2019. Influence of pyrolysis parameters on phosphorus fractions of biosolids derived biochar. Sci. Total Environ. 2019;695:133846. https://doi.org/10.1016/j.scitotenv.2019.133846
16. Lehmann J. Bio-energy in the black. Front. Ecol. Environ. 2007;5:381-7. https://doi.org/10.1890/1540-9295(2007)52.0.CO;2.
17. Figueiredo CC, Reis ASP, de Araujo AS, Blum LEB, Paz-Ferreiro J. Assessing the potential of sewage sludge-derived biochar as a novel phosphorus fertilizer: Influence of extractant solutions and pyrolysis temperatures. Waste Manage. 2021;124:144-53. https://doi.org/10.1016/j.wasman.2021.01.044.
18. Fachini J, Figueiredo CC, Frazão JJ, Rosa SD, da Silva J, do Vale, AT. Novel K-enriched organomineral fertilizer from sewage sludge-biochar: Chemical, physical and mineralogical characterization. Waste Manage. 2021:135:98-108. https://doi.org/10.1016/j.wasman.2021.08.027.
19. Li F, Liang X, Niyungeko C, Sun T, Liu F, Arai Y. Effects of biochar amendments on soil phosphorus transformation in agricultural soils. Adv. Agron. 2019;158:131-72. https://doi.org/10.1016/bs.agron.2019.07.002.

20. Cajamarca SMN., Martins D, da Silva J, Fontenelle MR, Guedes IMR, de Figueiredo CC, et al. Heterogeneity in the chemical composition of biofertilizers, potential agronomic use, and heavy metal contents of different agro-industrial wastes. Sustainability. 2019;11:1995. https://doi.org/10.3390/su11071995.
21. Chagas JKM, Figueiredo CC, Silva J, Shah K, Paz-Ferreiro J. Long-term effects of sewage sludge-derived biochar on the accumulation and availability of trace elements in a tropical soil. J. Environ. Qual. 2020;50:1-14. https://doi.org/10.1002/jeq2.20183.
22. Yuan H, Lu T, Hongyu H, Zhao D, Kobayashi N, Chen Y. Influence of pyrolysis temperature on physical and chemical properties of biochar made from sewage sludge. J. Anal. Appl. Pyrolysis. 2015;112:284-9, 2015. https://doi.org/10.1016/j.jaap.2015.01.010.
23. Council of the European Union. Council directive 86/278/EEC of 12 June 1986 on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture. Official Journal of the European Communities. 1968;181:6–12.
24. International Biochar Initiative (IBI). Standardized product definition and product testing guidelines for biochar that is used in soil. Available at: <http://www.biocharinternational.org/wpcontent/uploads/2018/04/IBI_Biochar_Standards_V2.1_Final.pdf>
25. Figueiredo CC, Chagas JKM, da Silva J, Paz-Ferreiro, J. Short-term effects of a sewage sludge biochar amendment on total and available heavy metal content of a tropical soil. Geoderma. 2019;344:31-9. https://doi.org/10.1016/j.geoderma.2019.01.052.
26. Cybulak M, Sololowska Z, Boguta P, Tomczyk A. Influence of pH and grain size on physicochemical properties of biochar and released humic substances. Fuel. 2019;240:334-8. https://doi.org/10.1016/j.fuel.2018.12.003.
27. Wang J, Liao Z, Ifthikar J, Shi L, Chen Z, Chen Z. One-step preparation and application of magnetic sludge-derived biochar on acid orange 7 removal via both adsorption and persulfate based oxidation. R. Soc. Chem. 2017; 7:18696-706. https://doi.org/10.1039/C7RA01425B.
28. Shen T, Tang Y, Lu XY, Zhen M. Mechanisms of copper stabilization by mineral constituents in sewage sludge biochar. J. Clean. Prod. 2018;193:185-93. https://doi.org/10.1016/j.jclepro.2018.05.071.
29. Hsu D, Lu C, Pang T, Wang Y, Wang G. Adsorption of ammonium nitrogen from aqueous solution on chemically activated biochar prepared from sorghum distillers grain. Appl. Sci. 2019;9:e5249. https://doi.org/10.3390/app9235249.
30. Karim AA, Kumar M, Singh SK, Panda CR, Mishra BK. Potassium enriched biochar production by thermal plasma processing of banana peduncle for soil application. J. Anal. Appl. Pyrolysis. 2016;123:165-72. https://doi.org/10.1016/j.jaap.2016.12.009.
31. Weber K and Quicker P. Properties of biochar. Fuel. 2018;217:240–61. https://doi.org/10.1016/j.fuel.2017.12.054.
32. Huang HJ, Yang T, Lai FY, Wu GQ. Co-pyrolysis of sewage sludge and sawdust/rice straw for production of biochar. J. Anal. Appl. Pyrolysis. 2017;125:61–8. https://doi.org/10.1016/j.jaap.2017.04.018.
33. Wang YY, Lu HH, Liu YX, Yang SM. Ammonium citrate-modified biochar: An adsorbent for La(III) ions from aqueous solution. Colloids Surf. A Physicochem. Eng. Asp. 2016;509:550–63. https://doi.org/10.1016/j.colsurfa.2016.09.060.
34. Antille D, Sakrabani R, Tyrrel SF, Le MS, Godwin RJ. Characterization of organomineral fertilizers nutrient-enriched biosolids granules. Appl. Environ. Soil Sci. 2013;e694597. https://doi.org/10.1155/2013/694597.
35. Gao Y, Xu S, Yue Q, Ortaboy S, Gao B, Sun Y. Synthesis and characterization of heteroatom-enriched biochar from keratin-based and wasted. Adv. Powder Tech. 2016;27:1280-6. https://doi.org/10.1016/j.apt.2016.04.018.
36. Chagas JKM, Figueiredo CC, Silva J, Paz-Ferreiro J. Sewage sludge biochars effects on corn response and nutrition and on soil properties in a 5-yr field experiment. Geoderma. 2021;401:e115323. https://doi.org/10.1016/j.geoderma.2021.115323.