



III *Sustentare* – Seminários de Sustentabilidade da PUC-Campinas
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PYROLYSIS OF SEWAGE SLUDGE: FROM UNWANTED WASTE TO DESIRED MATERIAL

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Abstract

Sewage sludge is a residue produced in large quantities and it is undesirable by virtue of its pathogens and potentially toxic components content, being difficult to find destination with low impacts in environment or human and animal health. In addition, Brazilian sewage sludge presents high inorganic composition, such as phyllosilicates and oxy-hydroxides of Fe, Al and Ti, resulting in complex reactions with organic matter. Here, we propose the pyrolysis of Brazilian sewage sludge to obtain biochar, bio-oil and biogas that are value added products. A pilot scale pyrolyser was built to thermally decompose sewage sludge in bio-char, bio-oil and biogas. Final temperature of pyrolysis promoted specific characteristics of biochar and modifications in the relative production of bio-oil and biogas, which serve as biofuels. Furthermore, it was possible to modify the biochar relative content of volatile matter, fixed carbon and ash, preserving or decomposing surface functional groups. It is possible to change biochar net surface electric charge and surface area, thus modifying water relations, such as pH, buffer-ing power, hydrophobicity and water retention. Oriented pyrolysis of sewage sludge by temperature control can promote strategies for waste disposal, decarbonization of the atmosphere, and energetic transition, promoting sustainable economic development.

Keywords: oriented pyrolysis, waste disposal, thermal decomposition, carbon sequestration, sanitation.

1. Introduction

The treatment of sewage generates sewage sludge, which is a residue of complex disposal. Due to the large volume and complexity of this pollutant waste, worldwide numerous researches (Alves et al., 2021; Xiao et al., 2022; Godlewska e Oleszczuk, 2022; Yang et al., 2022; Chen et al., 2022; Yu et al., 2022) are focused on its environmentally correct destination by means of pre-treatment, modifications and extraction of composites after intense characterization. In Brazil, sewage sludge has the peculiar profile of high ash content (Languer et al., 2020; Fachini et al., 2021), demanding investigation for its conversion in products of high added value.

In 2019, for example, approximately 49% of sanitary sewage was treated in Brazil, and with the possible expansion of basic sanitation, there is potential to double the production of sewage sludge (SNIS, 2019). Therefore, alternatives are sought to dispose of the sewage sludge, among them are landfills, incineration, addition in construction materials or deposition in soils (Samolada and Zabaniotou, 2014). Of these alternatives, all have some strong disadvantages, such as the shortage of landfill space, the concentration of toxic elements in incineration ashes, the reduction of the physical quality of construction materials mixed with sewage sludge, and



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the impacts in environment and human and animal health when this waste is incorporated into the soil. These impacts arise from the large mass produced, the presence of pathogens, and its content of potential toxic materials.

The pre-treatment that can reduce the mass of sewage sludge, eliminate pathogens and stabilize toxic materials is pyrolysis, which in turn is based on heating biomass in an inert atmosphere under temperature that volatilizes the compounds of low boiling point and transform the chemical species, resulting in chemical stability. The solid that is not volatilized is called biochar, which has a carbonaceous aspect, and the volatiles are derived into condensable and non-condensable, that give rise to bio-oil and biogas, respectively. The addition of value to sewage sludge by pyrolysis lies in the biological safety through thermal sterilization, the stabilization and fixation of carbon, and the potential of volatiles to be used as biofuels.

The challenges of sewage sludge pyrolysis are its high variability due to the different human activities that generate the sewage and the different treatments that generate the sewage sludge. Another challenge is the presence of a large amount of inorganic material in the Brazilian sewage sludge, which can come from the inorganic waste deposited in the sewage system, the soil that is carried along with the rainwater drained from the cities, and the sand used in the sewage sludge drying beds. During the heating of sewage sludge several transformations of organic and inorganic material occur simultaneously, giving uncertainty of the reactions occurring in the pyrolysis. Even though, it is known that the factor that has the greatest influence on the thermochemical transformation and the resulting characteristics of biochar and volatiles is the final temperature of heating.

In possession of information of the destination of sewage sludge it is possible to determine the pyrolysis temperature that maximizes some characteristic of interest. For example i) the fixation of carbon in the biochar during pyrolysis can serve as a tool to obtain carbon credits, ii) during pyrolysis all the moisture in the sewage sludge is removed, which is around 50 to 70%, doubling or even tripling the efficiency of logistics in transporting the solids, iii) the production of bio-oil and biogas can serve as biofuel, collaborating with the transition from fossil fuels to renewable fuels; iv) the devolatilization increases the porosity of biochar, enabling its use as a sorbent. Thus, this work aimed to study the influence of the pyrolysis temperature of sewage sludge on the fractions of solid and volatile products and on the characterization of biochar. It is expected that the results of this study will collaborate with strategies for waste disposal, decarbonization of the atmosphere, energy transition, and promote sustainable economic development.

2. Theoretical ground

The liquid waste from human activity is collected by the sewage system forming the sanitary sewage. The units responsible for the reception, treatment of sanitary sewage and effluent disposal are the Sewage Treatment Plants. The rules regarding collection, treatment of sanitary sewage and disposal of effluents in Brazil are set forth in the National Policy of Water Resources implemented by the National Agency of Waters and Basic Sanitation (ANA), part of the National System of Water Resources Management (Singreh), described in the new legal framework of sanitation, law No. 14.026, of July 15, 2020.



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There are many variations of sanitary sewage treatment process for its disposal, however most follow the flow of a primary treatment for removal of large objects, sedimentation of solids, suspension of oils and grease, and decantation of suspended organic solids forming the primary sewage sludge. Then follows the secondary treatment by biological digestion of the primary sewage sludge forming secondary sewage sludge. When the receiving water body should not receive elements and pollutants that are not removed by the secondary treatment, tertiary treatment based on physicochemical methods, such as filtration, ion exchange, reverse osmosis, and chlorination, is performed (Syed-Hassan et al., 2017).

When separating sewage sludge from the effluent by settling, it has moisture greater than 90% and has a liquid appearance. The most commonly used alternatives in reducing the moisture of sewage sludge are draining, centrifuging, and pressing (Syed-Hassan et al., 2017). A study performed in the state of Paraná reports that drainage was the most efficient technique in reducing moisture to values close to 50%, which technique is largely applied (Bittencourt et al., 2014). Sewage sludge passes from the liquid state to the solid state when the moisture is brought down to values lower than 70%, making it possible to be transported to Sludge Management Units for treatment and disposal.

Due to the retention of various contaminants in the sewage sludge that were present in the sanitary sewage, it has potentially toxic elements, high levels of pathogens, and contaminants that are persistent in the environment. The physical, chemical, and biological characteristics of sewage sludge have high variability depending on the human activity that generates the waste, the technology employed in the treatment of sanitary sewage, the standards of the effluent that is discharged to the receiving water body, and the post-treatment of the sewage sludge. Some practices for sewage sludge disposal are landfilling, incineration, addition to civil construction or application to agricultural soils (Bittencourt et al., 2014).

The disposal of sewage sludge to landfills can cause rapid exhaustion of space due to the large amount generated by urban centers, and incineration emits greenhouse gases and concentrates potentially toxic elements in the ash, generating a new waste that is difficult to dispose of (Samolada and Zabaniotou, 2014). The addition of sewage sludge in building materials, such as in brick manufacturing (Liew et al., 2003), is limited to small amounts as it can reduce the density and compressive strength of the material. The application of sewage sludge to agricultural soils has the potential to take advantage nutritional elements and increase soil organic carbon. However, sanitization of the sewage sludge prior to application is mandatory due to the danger of biological contamination (Bittencourt et al., 2017; Bittencourt, 2018).

The most effective option for sanitization and stabilization of sewage sludge is by thermal treatment, and the most promising technology is pyrolysis. In this process, heating is performed in an inert atmosphere to avoid combustion of the material. Pyrolysis is superior to other thermal treatments due to the transformation of sewage sludge into products with added value, such as the stable and sanitized solid called biochar and the products bio-oil and biogas, which have the potential to be used as biofuels (Samolada and Zabaniotou, 2014). Another advantage is the possibility of controlling the characteristics of the products obtained through different factors during pyrolysis, such as temperature, residence time, control of the atmosphere composition, catalysts, and the addition of other biomasses with the sewage sludge.



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The thermochemical transformation of biomass through heating in an inert atmosphere can be summarized by the following reaction:

Source material → Biochar + volatile (condensable + non-condensable)

Condensable volatiles when cooled give rise to bio-oil, while non-condensable volatiles give rise to biogas. Different pyrolysis conditions can increase or decrease the proportion of products. Slow pyrolysis, i.e. at a low heating rate, tends to increase the production of biochar, while fast pyrolysis tends to increase the production of volatiles (Demirbas and Arin, 2010). The heating rate to differentiate fast pyrolysis from slow pyrolysis is subjective and depends on the composition of the source material. For example, materials with high amounts of thermoresistant carbon or high amounts of thermally inert material tend to produce low amounts of volatiles even under heating rates considered high for other materials.

The thermal decomposition of sewage sludge can be divided into different phases, the most notable is dehydration in which water is removed, then decomposition of easily volatilizable materials in which devolatilization of low ebullition point materials occurs, and finally devolatilization and transformation of thermoresistant materials (Naqvi et al., 2019). Due to the high constitutional variability of Brazilian sewage sludge, the mechanisms of thermal decomposition and transformation become complex and difficult to predict, mainly because of the high variability of the organic material and the high amount of ash that can come from different inorganic materials (Oliveira Silva et al., 2012; Figueiredo et al., 2018; Naqvi et al., 2019; Languer et al., 2020).

The identification of different patterns of sewage sludge behavior during pyrolysis has led to differentiation between high ash or high organic matter sewage sludge (Alves et al., 2020). The inorganic composition of Brazilian sewage sludge is mostly mineral, explaining the atypical behavior compared to those with higher organic matter (Zielińska et al., 2015). Several reactions can occur at the same time during pyrolysis, such as dehydroxylation and transformation of mineral phases and interactions with organic matter (Rouquerol et al., 1975; Kustova et al., 1991; Ptáček et al., 2011; Redaoui et al., 2017). It is expected that Brazilian sewage sludge inherit more characteristics of minerals from highly weathered soils, such as 1:1 minerals, and 0:1 minerals such as kaolinite and iron, aluminum, and titanium oxhydroxides (Melo et al., 2001; Schaefer et al., 2008; Oliveira et al., 2020). Thus, comprehensive analyses of sewage sludge responses to thermal treatment are needed for the integration of pyrolysis in its treatment and disposal (Wang et al., 2022). Furthermore, the improvement of steps and processes, as well as the development of feasible and low-cost technologies, should be considered as primary requirements for the advancement of research in this area.

3. Methodology

3.1. Sewage sludge pyrolysis

For the sewage sludge pyrolysis procedure a carbon steel pyrolyzer was built in pilot scale, which is composed of an oven heated by liquefied petroleum gas (LPG) combustion, a fixed



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reactor with insulated atmosphere, and a gas conduction and cooling system for volatile condensation. The non-condensable volatiles are derived in a second pipeline and immediately combusted.

The thermodecomposition of sewage sludge by pyrolysis was performed in triplicates at temperatures of 300, 400 and 500 °C and with residence time of 2 hours, loading of 7 kg and heating rate of 5 °C min⁻¹. The mass of sewage sludge supplied and the mass of biochar, bio-oil and biogas products were monitored, being:

$$\text{Biogas (\%)} = 100 - \text{Biochar (\%)} + \text{Bio-oil (\%)}$$

where the mass of biogas produced was obtained by deduction of biochar and bio-oil from sewage sludge based on the conservation of mass.

3.2. Characterization of biochar

The biochar obtained from the different pyrolysis temperatures coded by the letter B plus the temperature. They were B300, B400 and B500 for the pyrolysis temperatures of 300, 400 and 500 °C, respectively.

3.2.1. Proximate and immediate analysis

The volatile material content, fixed carbon and ash were obtained by simultaneous thermogravimetric, differential thermogravimetry and exploratory calorimetry analysis (TGA/DTA/DSC) in 4 heating and cooling ramps, with a supply of 10 to 20 mg: 1st) in inert atmosphere, biochar was heated up to 140 °C at the rate of 50 °C min⁻¹ and left isothermal for 3 minutes; 2nd) heating ramp was performed at the rate of 100 °C min⁻¹ up to 950 °C and left isothermal for 3 minutes; 3rd) cooling was performed at the rate of -50 °C min⁻¹ up to 500 °C; 4th) the atmosphere was replaced to synthetic air and heating was performed at the rate of 100 °C min⁻¹ up to 800 °C and left isothermal for 3 minutes. The mass and enthalpy variations help in determining the transition of the reactions. The proximate composition was reported on a dry basis (García et al., 2013).

The C, H, and N elements of the particles were determined by ignition in a CHN model 2400 Serie II analyzer (Perkin Elmer, BR). The oxygen content was obtained from the deduction of the total mass of the other elements by calculating:

$$\text{O (\%)} = 100 - \text{C (\%)} + \text{H (\%)} + \text{N (\%)} + \text{Ash (\%)}$$

where O% is the oxygen composition of the material, C%, H%, N% and Ash% are the mass based fractions of the components C, H, N and ash.

3.2.2. Surface Characterization



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The surface functional groups and their evolution with temperature were characterized by Fourier transform infrared spectroscopy (FTIR). The sample pellet pressed in KBr (1%) was analyzed in a spectrometer model IRPrestige-2 (Shimadzu, BR) in the range of 4000 to 400 cm^{-1} with resolution of 2 cm^{-1} , with convergence of 128 scans and background correction with pure KBr pellet. Peak assignments in the interferogram were obtained by literature review.

Characterization of the topographic surface of the particles was obtained by scanning electron microscopy with a MIRA3 model electron microscope (Tescan, CZ). The samples were sieved on a 250 μm mesh and the particles were coated with gold. A voltage of 15 kV was applied for electron imaging.

The specific surface area of biochar was obtained by saturation with N_2 at the liquefaction point (77 K) and desorption in a NOVAtouch specific surface area analyzer (Antoon-Paar, AT). Specific surface area determination was performed by the Brunauer-Emmett-Teller (BET) method.

The net colloidal electric charge and its dynamic behavior with pH was characterized by zeta potential (ζ) in Zetasizer Nano ZS90 (Malvern, NL). Samples were sieved on 500 μm mesh and were suspended in 100 mL ultrapure water by sonification for 30 min at 110 W power and 40 KHz frequency in an ultrasonic washer model Eco-sonics (Prismalab, BR). To obtain particles smaller than 2 μm the suspension was left to decant with time calculated by Stokes' law estimating solids density of 1 to 1.5 kg m^{-3} . The ratio of ζ and pH was obtained by reducing the pH of the solution to 3 with 0.1 M L^{-1} of HCl and then was gradually raised to 8 in steps of 0.2 by adding drops of 1.68 μL of 0.1 M L^{-1} HCl using a precision titrator model MPT-2 (Malvern, NL).

3.2.3. Water relations

The water relations of biochar were studied as the humidity (m/m) and water potential relationship. The moisture at 1.5 MPa water potential was determined by the WP4-C dew point temperature water potential analyzer (Leong; Tripathy; Rahardjo, 2003) using the following calculation:

$$W_p = W_m \times \ln(-1000/\Psi_p) / \ln(-1000/\Psi_m)$$

where W_p is the moisture content of the sample at the potential Ψ_p to be calculated and W_m is the moisture content at the potential Ψ_m obtained by evaporating the sample in a natural environment until the closest value to the moisture content to be calculated.

The hydrophobicity of biochar was determined by solid-liquid interaction with droplet deposition on the surface (Letey; Carrillo; Pang, 2000). The sample was sieved on 500 μm mesh and serial dilution of absolute ethyl alcohol in water was performed. The sample was dried at 105 $^\circ\text{C}$ and about 4 g of sample was pulverized onto watch glass. A drop of approximately 50 μL of each alcohol dilution was deposited on the sample. The persistence of hydrophobicity was measured by the absorption time of a 50 μL drop of deionized water on approximately 3 g



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of sample sprayed on a glass slide. The absorption time of 8 drops was recorded and the average result was given at 1-hour intervals.

The pH and electrical conductivity of the hydrated samples were studied by diluting 2.5 g of sample in 25 mL of deionized water (Richards, 1954). The sample was stirred on an orbital table at 250 rpm for 1 hour and allowed to stand for 1 hour. The pH and electrical conductivity (EC) of the sample were determined after resting.

4. Results

4.1 Sewage sludge pyrolysis

The sewage sludge had 6.7% moisture and 49.8% ash, so it was expected to collect a minimum of 620 mL of condensable material in the collector from dehydration. The decomposable mass supplied was 3.20 kg (dry mass minus ash) and the dry mass was 6.53 kg. When observing the biochar, darkening, cracking, and reduced aggregation were identified (Figure 1).

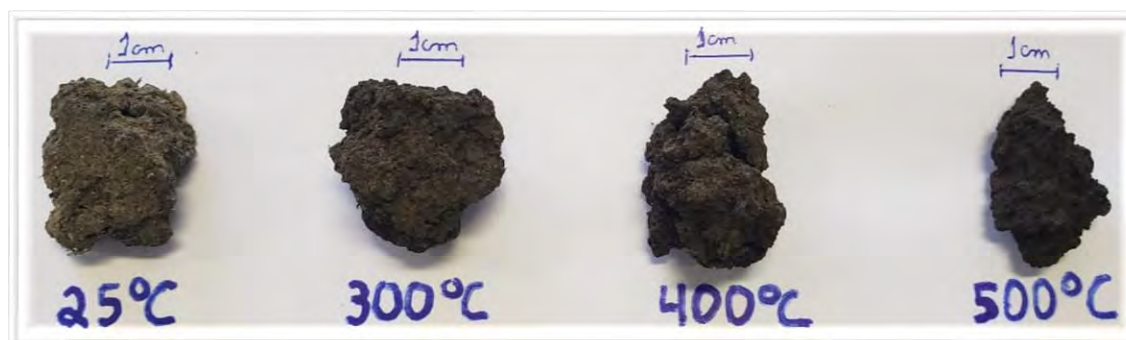


Figure 1. Illustration of sewage sludge and biochar aggregates from different temperatures.

The average results observed for the different pyrolysis temperatures are presented in Table 1. The increase of devolatilization of sewage sludge with the increase of pyrolysis temperature resulted in the reduction of biochar mass and the increase of mass of volatiles such as bio-oil and biogas. Deducting the initial moisture of the sewage sludge of 6.7%, the decomposition of solids was equal to 5.3, 13.9 and 23.7% with the respective increase in temperature.

Table 1. Relative fractions of pyrolysis products at different temperatures.

Temperature (°C)	Biochar ----- (%) -----	Bio-oil ----- (%) -----	Biogas
300	88.0	11.2	0.8
400	79.4	18.0	2.6
500	69.6	25.1	5.3



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4.2 Characterization of biochar

4.2.1 Proximate and immediate composition

There was a reduction of volatile material (VM) with the increase of pyrolysis temperature in which the heat flux of devolatilization decreased with the increase of pyrolysis temperature up to 400 °C and when the biochar was obtained at 500 °C the enthalpy increased (Table 2). The fixed carbon (FC) showed a behavior directly related to the increase of temperature. The heat flux during the combustion of FC increased until the biochar obtained at 400 °C and decreased when obtained at 500 °C. The variations of heat flux occurring in pyrolysis at 500 °C may be related to the aromatization of carbon with low crystallinity, which increases the FC and reduces the enthalpy, implying that FC might have a shorter half-life. The ash (A) content increased with increasing temperature and should be mostly related to the persistence of inorganic materials of high boiling point such as minerals and trace elements.

Table 2. Proximate composition of sewage sludge and biochar obtained at different pyrolysis temperatures and heat flux of thermal removal of the different compositions.

Material	VM	FC	A	VM	FC
	----- (%) -----			---- (Wg ⁻¹) ----	
Sewage sludge	39.6	4.8	55.6	15.2	3.5
B300	35.9	5.7	58.3	13.5	6.9
B400	32.2	7.7	60.1	12.4	9.4
B500	25.4	9.4	65.2	13.6	7.7

The composition of the elements C, H, N and O (Table 3) are changed in a non-linear aspect with pyrolysis temperature. It was observed an increase of C and H and reduction of N and O of the biochar obtained at 300 °C in relation to sewage sludge. The different reactions of the organic and inorganic material may be related to the non-linearity, for example the transition of goethite (FeOOH) into hematite (Fe₂O₃) or of gibbsite (Al(OH)₃) into boehmite (AlO(OH)) that occur between 200 and 300 °C and the volatilization of volatile carbon species above 300 °C. These reactions are suggestive that the relative increase in O must occur because it is part of the crystalline ordering of the mineral-forming metals.

Table 3. Composition of elements and atomic ratios.

Material	C	H	N	O	H/C	O/C	N/C
	----- (%) -----						
Sewage sludge	25.7	4.4	3.1	11.1	0.17	0.43	0.12
B300	27.6	4.5	3.0	7.5	0.16	0.27	0.11
B400	24.4	3.3	2.6	9.4	0.13	0.39	0.11
B500	18.1	2.4	2.2	12.1	0.13	0.67	0.12



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The elemental change had an effect on the atomic ratios. The reduction of the H/C ratio is an indicator of increased π -bonding between carbons and possible formation of aromatic carbons with higher number of rings, and can be used as an indicator of the persistence of the carbon in the environment. The evolution in the structure of biochar with temperature can also change the thermodynamics of element sorption, especially cationic metals that are weak Lewis acids, such as Cd, Pb, Zn, Ti due to the affinity of the π -bonds with such metals. The increase of the O/C ratio with temperature is likely to be linked to the effect of persistence of oxygen in the structure of the minerals and volatilization of C species. The initial reduction of N/C may be linked to the decomposition of primary and secondary amides and the subsequent increase may be related to the formation of nitrides, which come from the deposition of metals on organic matter.

4.2.2 Surface characterization

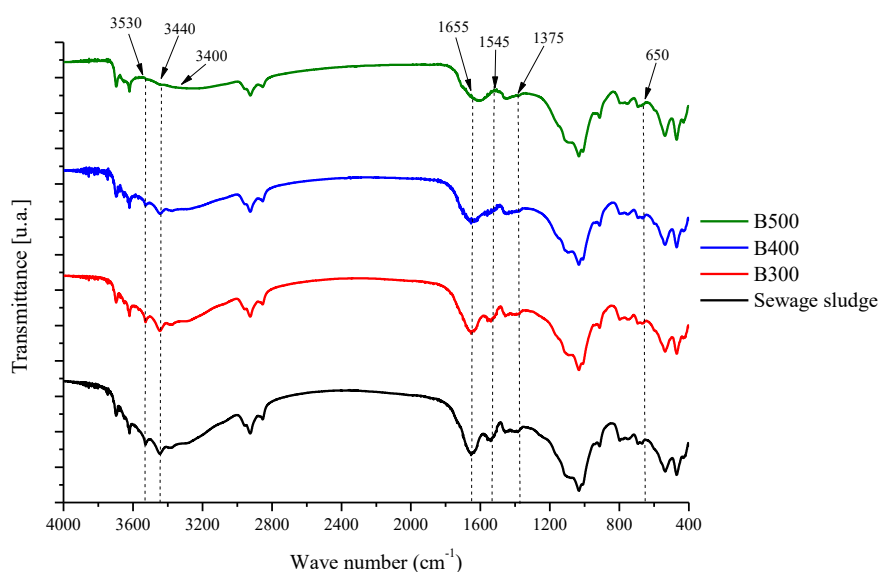


Figure 2. Interferogram of sewage sludge and biochar.

The FTIR analysis (Figure 2) is complex and shows several organic and inorganic functional groups. The main temperature related transitions are reducing peaks at 3450 cm^{-1} , 3440 cm^{-1} , 1655 cm^{-1} , 1545 cm^{-1} , 1375 cm^{-1} and 540 cm^{-1} . The peak at 3530 cm^{-1} is assigned to the hydroxyl functional group (-OH) and at 650 cm^{-1} the silanol bond (Si-O) and are related to dehydroxylation of silicate minerals (Bukalo et al., 2017; Figueiredo et al., 2018). The reduction of the peak at 3440 cm^{-1} and 1545 cm^{-1} from 400 °C and disappearance at 500 °C indicates the decomposition of secondary amides and the broadening of the peak at 1655 cm^{-1} is related to the transition of primary amides into nitrogen-containing heterocyclic carbon (Liu et al., 2017). It is possible that the formation of nitrides (MN_x) occurs at temperatures near 400 °C by the persistence of the peak at the position at 1440 cm^{-1} , complexing metals present in sewage sludge



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(Sugiyama et al., 1975). The reduction of the peak at 1375 cm^{-1} indicates depolymerization and some authors suggest that this effect is linked to the reduction of polycyclic aromatic hydrocarbons (PAHs), which are compounds with toxic potential and their decomposition indicates safety of biochar handling (Khan et al., 2013; Waqas et al., 2014; Waqas et al., 2015; Li et al., 2017).

In summary, FTIR analysis indicates that upon pyrolysis at 300 °C there is persistence of carbon functional groups and dihydroxylation. At temperatures of 400 °C and 500 °C a complex of reactions occur as transition of carbon species with the formation of heterocyclic carbon and nitrides, depolymerization of polycyclic carbon, inheritance of thermoresistant aliphatic or aromatic carbon, and dehydroxylation of minerals. These reactions are consistent with the enthalpy from the TGA/DTA/DSC analysis used in the determination of VM and FC (Table 2), in which the enthalpy showed a transition between 400 °C and 500 °C , probably related to the transformation of carbon species. With this information it is possible to perform pyrolysis engineering to obtain biochar preserving the functional groups or increasing the fixed carbon and complexing metals.

The topographic surface of the particles is heterogeneous and lumpy. With the increase of temperature the most obvious transition is the dispersion of the particles and the increase of cracks in the faces of the aggregates, mainly in the biochar obtained at 500 °C (Figure 3). These characteristics may be important in increasing the specific surface area and sorption capacity of biochar. The surface area obtained by the BET method was $5.2\text{ m}^2\text{ g}^{-1}$; $5.6\text{ m}^2\text{ g}^{-1}$; $5.4\text{ m}^2\text{ g}^{-1}$ and $11.5\text{ m}^2\text{ g}^{-1}$ for sewage sludge and biochar from 300 °C to 500 °C , respectively. The surface area transition of biochar is negligible when pyrolysed up to 400 °C and has an expressive increase when practiced at 500 °C . This effect is complex and seems to involve at the same time the removal of volatile material giving way to new pores and transformation of the mineral phase reducing the specific surface area.

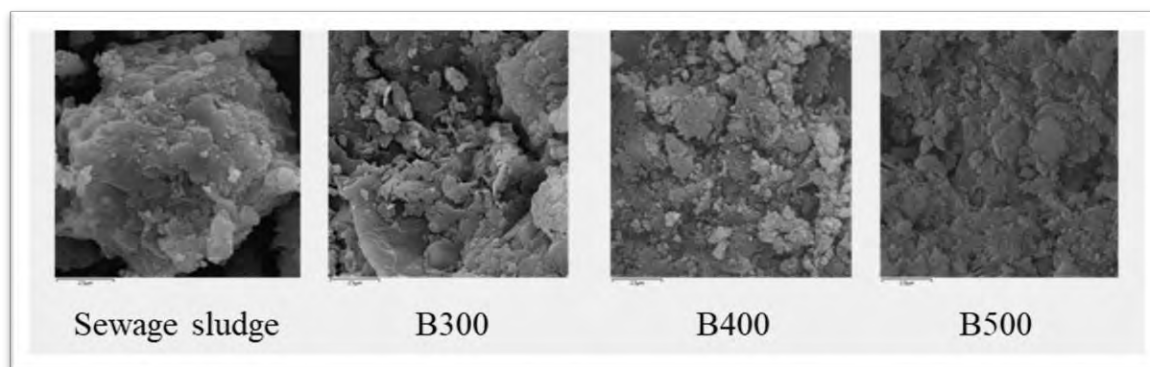


Figure 3. Electron images of sewage sludge and biochar at 17,000 x magnification.

The relationship of ζ and pH obtained from the material is plotted in Figure 4. The ζ was reduced between the sewage sludge and the biochar obtained at 300 °C and then there was inverse relationship of the pyrolysis temperature increment with the net surface charge. It is



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possible that the decomposition of positively charged material such as gibbsite, goethite and amides have a greater influence on the formation of net negative charge in this biochar than the formation of negatively charged carbon species.

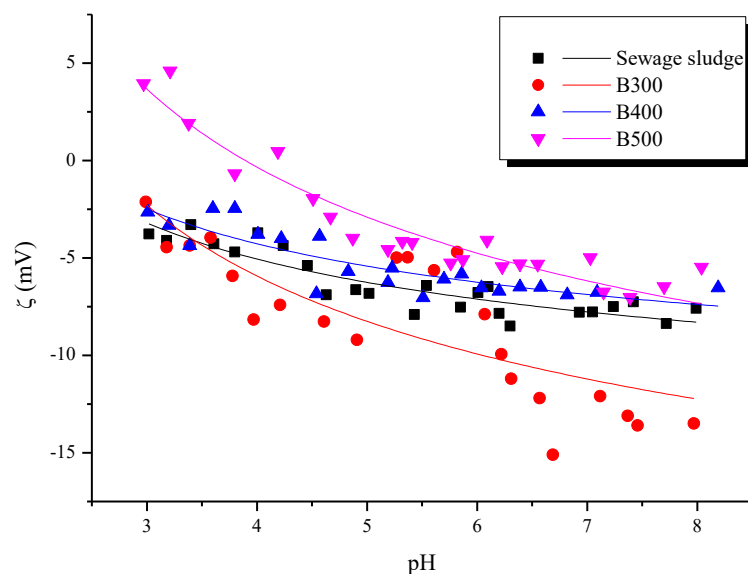


Figure 4. Evolution of ζ as a function of solution pH of the different samples.

The pyrolysis above 300 °C must have increased negative electric charges due to the dihydroxylation of material that forms positive charge, as gibbsite and goethite, resulting in more negative net charge. The biochar obtained at 500 °C showed an isoelectric point at pH 3.9, which is consistent with the decomposition of kaolinite and the persistence of thermoresistant nitrides and amides, which are positively charged. At the higher pH range there are negative electrical charges in the 500 °C biochar, but the identification of zero net charge and positive net charge is consistent with the reduction of strong Lewis acid groups relative to weakly acidic and basic groups.

4.2.3 Water relations

The water adsorbed at 1.5 MPa is associated with the phenomenon of capillarity, which consists of the ability to retain water physically and chemically through the density of electric charges, the porous structure of the material, and the solid-liquid contact angle, which represents the capacity for water intrusion into the porous material, as suggested by Thomas Young's theory (1805). The contribution of these characteristics seems to have been synergistic at the temperature of 300 °C (Table 4), which presented the highest water retention. With the increase in pyrolysis temperature, there was a reduction in water retention. All treatments presented hydrophobicity (>90°), and the solid-water contact angle increased for sewage sludge compared to biochar obtained at different temperatures and the hydrophobicity resistance was inversely proportional to the pyrolysis temperature.



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Table 4. Water retention, solid-water contact angle and hydrophobic resistance.

Material	Water retention at 1,5 MPa (%)	θ (°)	Hydrophobic resistance (h)
Sewage sludge	20,8	112,4	3
B300	25,6	113,2	7
B400	21,9	113,2	11
B500	17,3	113,2	15

The increase in pyrolysis temperature caused a reduction in electrical conductivity. The increase in pyrolysis temperature seems to increase the sorption of metals in the biochar, making them non-exchangeable with the solution and reducing the EC. All treatments presented acidic character ($\text{pH} < 7$) and the increase in pyrolysis temperature increased the pH of the biochar suspension when obtained from pyrolysis up to 400 °C. The biochar from sewage sludge presents promising characteristics to act as a buffering agent, since to increase the pH from 3 to 8 of the diluted biochar suspension obtained from pyrolysis at 300 °C it was necessary 0.515 mL of NaOH 0.1 M L⁻¹ solution in relation to 0.192 mL, 0.301 mL and 0.292 mL for the sewage sludge samples and biochar obtained at 400 °C and 500 °C, respectively. Therefore, the biochar obtained at 300 °C presents characteristics more similar to those of strong Lewis acids, while the others present characteristics closer to those of weak acids, because the pH is changed more easily. In the case of pyrolysis at 500 °C, the biochar presented PCZ in the pH range of study, implying that this material is the one with the greatest characteristic of weak acid in relation to the others.

1.1 5. Conclusions

The pyrolysis orientation by thermal control shows promise for the destination of sewage sludge in which it is possible to obtain some characteristics of biochar as desired. This practice has valorized a residue that is difficult to dispose of and has made it possible to obtain biogas and bio-oil that are promising for use as biofuels. The evolution of this research lies in the investigation of the risks of the application of biochar from sewage sludge, being possible to perform serial extractions of potentially toxic metals and *Escherichia coli* count.

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1.3 7. References

Alves, B. S. Q., Zelaya, K. P. S., Colen, F., Frazão, L. A., Napoli, A., Parikh, S. J., & Fernandes, L. A. (2021). Effect of sewage sludge and sugarcane bagasse biochar on soil properties and sugar beet production. *Pedosphere*, 31(4), 572–582. [https://doi.org/10.1016/S1002-0160\(21\)60003-6](https://doi.org/10.1016/S1002-0160(21)60003-6)

Alves, J. L. F., da Silva, J. C. G., Languer, M. P., Batistella, L., Di Domenico, M., da Silva Filho, V. F., Moreira, R. de F. P. M., & José, H. J. (2020). Assessing the bioenergy potential of high-ash anaerobic sewage sludge using pyrolysis kinetics and thermodynamics to design a sustainable integrated biorefinery. *Biomass Conversion and Biorefinery*. <https://doi.org/10.1007/s13399-020-01023-2>

Bittencourt, S. (2018). Agricultural Use of Sewage Sludge in Paraná State, Brazil: A Decade of National Regulation. *Recycling*, 3(4), 53. <https://doi.org/10.3390/recycling3040053>

Bittencourt, S., Aisse, M. M., & Serrat, B. M. (2017). Gestão do uso agrícola do lodo de esgoto: Estudo de caso do estado do Paraná, Brasil. *Engenharia Sanitaria e Ambiental*, 22(6), 1129–1139. <https://doi.org/10.1590/s1413-41522017156260>

Bittencourt, S., Serrat, B. M., Aisse, M. M., & Gomes, D. (2014). Sewage Sludge Usage in Agriculture: A Case Study of Its Destination in the Curitiba Metropolitan Region, Paraná, Brazil. *Water, Air, & Soil Pollution*, 225(9), 2074. <https://doi.org/10.1007/s11270-014-2074-y>

Chen, Y., Yi, L., Yin, J., Jin, H., & Guo, L. (2022). Sewage sludge gasification in supercritical water with fluidized bed reactor: Reaction and product characteristics. *Energy*, 239, 122115. <https://doi.org/10.1016/j.energy.2021.122115>

Demirbas, A., & Arin, G. (2010). An Overview of Biomass Pyrolysis. *Energy Sources*, 24(5), 471–482. <https://doi.org/10.1080/00908310252889979>

Fachini, J., Figueiredo, C. C. de, Frazão, J. J., Rosa, S. D., da Silva, J., & Vale, A. T. do. (2021). Novel K-enriched organomineral fertilizer from sewage sludge-biochar: Chemical, physical and mineralogical characterization. *Waste Management*, 135, 98–108. <https://doi.org/10.1016/j.wasman.2021.08.027>



III *Sustentare* – Seminários de Sustentabilidade da PUC-Campinas
VI WIPIS – Workshop Internacional de Pesquisa em Indicadores de Sustentabilidade
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Godlewska, P., & Oleszczuk, P. (2022). Effect of Biomass Addition Before Sewage Sludge Pyrolysis on the Persistence and Bioavailability of Polycyclic Aromatic Hydrocarbons in Biochar-Amended Soil. *Chemical Engineering Journal*, 429, 132143. <https://doi.org/10.1016/j.cej.2021.132143>

Kustova, G. N., Burgina, E. B., Sadykov, V. A., & Poryvaev, S. G. (1991). Vibrational spectroscopic investigation of the goethite thermal decomposition products. *Physics and Chemistry of Minerals*, 18(6). <https://doi.org/10.1007/BF00199419>

Languer, M. P., Batistella, L., Alves, J. L. F., Da Silva, J. C. G., da Silva Filho, V. F., Di Domenico, M., Moreira, R. de F. P. M., & José, H. J. (2020). Insights into pyrolysis characteristics of Brazilian high-ash sewage sludges using thermogravimetric analysis and bench-scale experiments with GC-MS to evaluate their bioenergy potential. *Biomass and Bioenergy*, 138, 105614. <https://doi.org/10.1016/j.biombioe.2020.105614>

Liew, A. G., Idris, A., Samad, A. A., Wong, C. H. K., Jaafar, M. S., & Baki, A. M. (2003). Reusability of sewage sludge in clay bricks. *Journal of Material Cycles and Waste Management*, 6(1), 41–47. <https://doi.org/10.1007/s10163-003-0105-7>

Melo, V. F., Singh, B., Schaefer, C. E. G. R., Novais, R. F., & Fontes, M. P. F. (2001). Chemical and Mineralogical Properties of Kaolinite-Rich Brazilian Soils. *Soil Science Society of America Journal*, 65(4), 1324–1333. <https://doi.org/10.2136/sssaj2001.6541324x>

Naqvi, S. R., Tariq, R., Hameed, Z., Ali, I., Naqvi, M., Chen, W.-H., Ceylan, S., Rashid, H., Ahmad, J., Taqvi, S. A., & Shahbaz, M. (2019). Pyrolysis of high ash sewage sludge: Kinetics and thermodynamic analysis using Coats-Redfern method. *Renewable Energy*, 131, 854–860. <https://doi.org/10.1016/j.renene.2018.07.094>

Oliveira Silva, J., Filho, G. R., da Silva Meireles, C., Ribeiro, S. D., Vieira, J. G., da Silva, C. V., & Cerqueira, D. A. (2012). Thermal analysis and FTIR studies of sewage sludge produced in treatment plants. The case of sludge in the city of Uberlândia-MG, Brazil. *Thermochimica Acta*, 528, 72–75. <https://doi.org/10.1016/j.tca.2011.11.010>

Oliveira, J. S., Inda, A. V., Barrón, V., Torrent, J., Tiecher, T., & de Oliveira Camargo, F. A. (2020). Soil properties governing phosphorus adsorption in soils of Southern Brazil. *Geoderma Regional*, 22, e00318. <https://doi.org/10.1016/j.geodrs.2020.e00318>



III *Sustentare* – Seminários de Sustentabilidade da PUC-Campinas
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16 a 18 de novembro de 2021

Ptáček, P., Šoukal, F., Opravil, T., Havlica, J., & Brandštetr, J. (2011). The kinetic analysis of the thermal decomposition of kaolinite by DTG technique. *Powder Technology*, 208(1), 20–25. <https://doi.org/10.1016/j.powtec.2010.11.035>

Redaoui, D., Sahnoune, F., Heraiz, M., & Raghdi, A. (2017). Mechanism and Kinetic Parameters of the Thermal Decomposition of Gibbsite Al(OH) 3 by Thermogravimetric Analysis. *Acta Physica Polonica A*, 131(3), 562–565. <https://doi.org/10.12693/APhysPolA.131.562>

Rouquerol, J. (1975). Thermal decomposition of gibbsite under low pressures I. Formation of the boehmitic phase. *Journal of Catalysis*, 36(1), 99–110. [https://doi.org/10.1016/0021-9517\(75\)90014-7](https://doi.org/10.1016/0021-9517(75)90014-7)

Samolada, M. C., & Zabaniotou, A. A. (2014). Comparative assessment of municipal sewage sludge incineration, gasification and pyrolysis for a sustainable sludge-to-energy management in Greece. *Waste Management*, 34(2), 411–420. <https://doi.org/10.1016/j.wasman.2013.11.003>

Schaefer, C. E. G. R., Fabris, J. D., & Ker, J. C. (2008). Minerals in the clay fraction of Brazilian Latosols (Oxisols): A review. *Clay Minerals*, 43(1), 137–154. <https://doi.org/10.1180/claymin.2008.043.1.11>

SNIS. Esgotamento sanitário 2019, 2019. Disponível em: <<http://www.snis.gov.br/painel-informacoes-saneamento-brasil/web/painel-esgotamento-sanitario>>

Syed-Hassan, S. S. A., Wang, Y., Hu, S., Su, S., & Xiang, J. (2017). Thermochemical processing of sewage sludge to energy and fuel: Fundamentals, challenges and considerations. *Renewable and Sustainable Energy Reviews*, 80, 888–913. <https://doi.org/10.1016/j.rser.2017.05.262>

Xiao, Y., Raheem, A., Ding, L., Chen, W.-H., Chen, X., Wang, F., & Lin, S.-L. (2022). Pre-treatment, modification and applications of sewage sludge-derived biochar for resource recovery- A review. *Chemosphere*, 287, 131969. <https://doi.org/10.1016/j.chemosphere.2021.131969>

Yang, X., Zeng, L., Huang, J., Mo, Z., Guan, Z., Sun, S., Liang, J., & Huang, S. (2022). Enhanced sludge dewaterability by a novel MnFe₂O₄-Biochar activated peroxymonosulfate process combined with Tannic acid. *Chemical Engineering Journal*, 429, 132280. <https://doi.org/10.1016/j.cej.2021.132280>



III *Sustentare* – Seminários de Sustentabilidade da PUC-Campinas
VI WIPIS – Workshop Internacional de Pesquisa em Indicadores de Sustentabilidade
16 a 18 de novembro de 2021

Yu, B., Xiao, X., Wang, J., Hong, M., Deng, C., Li, Y.-Y., & Liu, J. (2022). Enhancing phosphorus recovery from sewage sludge using anaerobic-based processes: Current status and perspectives. *Bioresource Technology*, 341, 125899. <https://doi.org/10.1016/j.biortech.2021.125899>

Zielińska, A., Oleszczuk, P., Charmas, B., Skubiszewska-Zięba, J., & Pasieczna-Patkowska, S. (2015). Effect of sewage sludge properties on the biochar characteristic. *Journal of Analytical and Applied Pyrolysis*, 112, 201–213. <https://doi.org/10.1016/j.jaap.2015.01.025>