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Investigation of cattle manure, poultry manure and sewage sludge as raw materials for biochar synthesis via pyrolysis: A case study for Küçük Menderes Basin-Türkiye

Piroliz yoluyla biyoçar sentezi için hammadde olarak inek gübresi, tavuk gübresi ve arıtma çamurunun incelenmesi: Küçük Menderes Havzası-Türkiye için bir vaka çalışması

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Abstract

Decomposition products from direct disposal of manure and sewage sludge have negative impacts on water resources, soil and atmosphere. Here, biochar synthesized from cattle and poultry manure and sewage sludge generated in the Küçük Menderes Basin (>6 million tons dw/year) by pyrolysis and the properties of the biochars were examined. TGA-DTA results showed that, the maximum weight losses realized in the range of 200-500°C. The loss of O-H stretching of hydroxyl groups and C-H stretching of aliphatic CH_x observed in the analysis of FT-IR results indicated the successful pyrolysis. Biochars synthesized from cattle and poultry manure at 700°C resulted in the largest BET surface areas (47.59 m^2/g and 11.31 m^2/g, respectively). The largest BET surface area for sewage sludge biochar was obtained at 500°C (41.76 m^2/g). This different result was found to be related to the melting of the high inert content of sewage sludge containing treatment chemicals at >500°C. SEM results supported the BET results and it was evaluated that the melted inert structure of the sludge partially trapped the biochar formed. It was concluded that, not only the volatile content of the wastes, but also the ratio and structure of their inert content are effective in biochar quality.

Keywords: BET, Biochar, FT-IR, Manure, SEM, Sewage sludge

Öz

Tarımsal ve kentsel alanlardan kaynaklanan hayvan gübresi ve arıtma çamuru gibi atıkların doğrudan bertarafı olumsuz çevresel etkiler yaratmaktadır. Çalışma kapsamında Küçük Menderes Havzasında oluşan ve yıllık toplam üretimleri 6 milyon ton kuru maddeye ulaşan inek ve tavuk atıkları ile arıtma çamurundan biyoçar üretimi ele alınmış ve piroliz yoluyla sentezlenen biyoçarların özellikleri incelenmiştir. TGA-DTA sonuçlarına göre malzemelerde kütlesel kayıpların en fazla 200-500°C aralığında olduğu belirlenmiştir. FT-IR sonuçları incelendiğinde, hidroksil gruplarının O-H gerilmesinin ve alifatiklerin C-H gerilmesinin kaybolması, numunelerin pirolizinin başarılı olduğunu göstermektedir. BET analizlerine göre inek ve tavuk gübresinden 700°C'de sentezlenen biyoçarlar en iyi BET yüzey alanı değerini verirken, arıtma çamurundan 500°C'de üretilen biyoçar en yüksek BET yüzey alanı değerini vermiştir. Bu farklılık, arıtma çamurunun bünyesinde kalan, >500°C'de ergiyen, yüksek inert içeriğe sahip arıtma kimyasalları ile ilişkili bulunmuştur. SEM sonuçları BET sonuçlarını destekler nitelikte olup, ergiyen inert içeriğin oluşan biyoçarı kısmen bünyesinde hapsettiği değerlendirilmiştir. İnek ve tavuk gübresi ile arıtma çamurundan biyoçar üretimi umut vadediyor olmakla birlikte daha ileri çalışmalar gerektirmektedir.

Anahtar kelimeler: Arıtma çamuru, Biyoçar, İnek gübresi, Piroliz, Tavuk gübresi

1 Introduction

As technology develops, people's consumption habits change and the amount of waste generated increases in general [1]. Waste generation is projected to increase from 2.24 billion tons in 2020 to 3.88 billion tons in 2050 [2],[3]. The amount of sewage sludge and animal manure produced, that should be managed properly, also increases, but thanks to new technology, the amount going to landfills is decreasing [4]. However, there is still a large amount that needs to be dealt with; it is estimated that 45 million tons of dry sludge were produced in 2018 globally, despite the exact amount not being known [5],[6]. Due to lack of legal and financial resources, sewage sludge management receives little attention in a significant part of the world. In 2018, 318.5 thousand tons of sewage sludge was produced in Türkiye, which decreased slightly to 314 thousand tons in 2020. Approximately 285 thousand tons of this amount was disposed of [7] via various disposal methods such as landfilling and incineration as the common practices [5]. While strict European laws prohibit landfilling of sewage sludge, in the United States 50% of sewage sludge is still sent to landfilling [8]. The European Union allows the use of sludge in agriculture if certain conditions are met [9]. In Europe, 36% of sewage sludge is incinerated, 33% is used in agriculture and 12% is composted, where only 8% is disposed of in landfills [7]. In the United States, about 35% of sewage sludge is used as fertilizer, while in Japan 70% of sewage sludge is incinerated. In addition, in South Korea, most of the sewage sludge is dumped into the sea [5]. In Türkiye, about a half of the sludge is incinerated (49%), 46% is sent to landfills, and 4% of the sludge is used in agriculture [7]. It is reported in many past researches that, landfilling and incineration are the methods increasing greenhouse gas emissions to the atmosphere, where the use of raw sludge is also increasing health risks of end-user farmers and the pesticides, heavy metals and other contaminants it may contain can contribute to the food chain

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[10]. In addition, the mobilization of nitrogen and phosphorus in sludge to deep into the Earth's crust may contaminate water sources [5]. In 2016, 9.9 million tons of animal manure was produced in Europe, which decreased to 9.6 million tons in 2018 while 88% of this amount is recovered, 6% is used for energy, 4% is incinerated and only 1% is sent to landfill [11]. In Türkiye, there has been no significant change in the number of farm animals in recent years [12], but there is still a large amount of animal manure to deal with [13]. Although animal manure is highly preferred for agricultural soil improvement, when it is stored and used in unappropriated conditions, it also has a potential to pollute water resources [13].

The conversion of biowaste to biochar through pyrolysis is an upcycling process and it has many environmental and economic benefits such as energy production, sustainable waste recycling, the immobilization of heavy metals and organic pollutants, carbon sequestration, soil quality improvement, stimulated plant growth and mitigating greenhouse gas emissions [5]. For the reasons listed above, biochar production from various materials such as crop residues, woody materials, green wastes, sewage sludge and animal manure has gained importance today, but it still requires more detailed studies as corresponding material properties vary so widely around the world [14]. Sewage sludge is primarily preferred for biochar production because it is a good source of carbon. The biochar of sewage sludge can be used for many useful activities especially increasing crop yield, improving the quality of the nutrient-deficient soils like acidic, dry and humid. Moreover, it can reduce the pollution of groundwater and surface water by holding the agrochemicals like nitrate and phosphate which can cause eutrophication and nitrate pollution [15]. Besides, application of biochar of manure to agricultural soils can increase soil organic carbon contents, soil fertility and crop productivity. Furthermore, it affects global warming by decreasing nitrous oxide (N_2O) emission while direct application of manure to soil results in the opposite [16]. Biochar is also rich in organic matter and nutrients so supports the growth of soil microorganisms [5],[14],[17]. Studies show that the use of biochar can reduce greenhouse gas emissions, nitrous oxide and methane release from soils to the atmosphere, which are contributing to the climate change, where biochar can mitigate climate change by reducing carbon dioxide pollutants in soils thanks to carbon sequestration [14]. In addition, pyrolysis of manures and sewage sludge is a very efficient method for volume reduction as well as for the removal of pathogens. The parameters to be applied during pyrolysis of these wastes vary according to the desired product [5],[14],[17].

In the studies conducted in Turkiye, biomass potential was mostly determined and the characterization of these wastes was not emphasized [18]-[20]. In addition, the effect of biochar applied to soil on plants was examined [21],[22]. Biochar was mixed with raw manure at various ratios and its effects on plant growth and yield were investigated [23],[24].

Küçük Menderes Basin in Türkiye has a high agricultural potential with its climate that allows product diversity, fertile plains, water resources and organizational structure. Moreover, İzmir is one of the important livestock raising centers of Türkiye and the region [25], where these activities are mainly conglomerated in Küçük Menderes Basin. However, non-point pollution in the large alluvial plains of the region is largely caused by the raw manure from raising livestock activities [26] along with the use of commercial fertilizers in agriculture. Besides these wastes, the region has another waste disposal problem of sewage sludge which should be handled carefully because of its toxicity and safety issues [15].

Manure and sewage sludge from the region have a potential to be used for energy obtain and for soil improvement in agricultural purposes [27]-[32]. The legal legislation also aims to prioritize the approach of bringing waste into the economy by using it for material or energy recovery and to reduce the amount of waste sent to landfill [33]. The European Union also aims to reduce the loss of raw materials by preventing waste from being sent to landfills according to the zero-waste program within the framework of waste and the circular economy. it supports the creation of new products by promoting energy recovery where necessary [34],[35]. Similar approaches are seen in the United States of America, which supports the production of new raw materials with energy recovery if the first steps in the waste hierarchy cannot be implemented [36]. Moreover, direct use of raw sludge in soil is prohibited in Türkiye [27]. The European Union also encourages the reuse of sewage sludge, provided that the necessary conditions are met, and aims to reduce its impact on the environment [37]. In the USA, it is stated that sewage sludge can be sent to landfill, land applied or incinerated according to the conditions specified in the standards for the use or disposal of sewage sludge (40 CFR Part 503) [38].

Here, the properties of sewage sludge and animal manure generated in Küçük Menderes Basin were investigated by means of their availability for biochar production. The biochar properties under different pyrolysis conditions and the surface properties of the final product were also determined to investigate the possibilities of feeding these wastes into the circular economy through an upcycling process.

2 Materials and methods

2.1 Study area

The Küçük Menderes Basin covers an area of 6,967 km^2 in western Türkiye, which empties its waters into the Aegean Sea with the Küçük Menderes River and other small streams [26]. In terms of land use, 40% of the basin consists of plains, while 75% of İzmir and its affiliated districts are within the basin [25],[26]. There are 34867 dairy farms in the region [39], and animal products have a share of 38.41% of Izmir's agricultural production where 37.8% of this rate is milk, 33.1% is white meat, 20.3% is red meat and 6.5% is egg in 2016 [25]. Milk production accounted for 5% of the overall milk production in Türkiye [40]. Moreover, there are 447 poultry farms [39].

Considering the number of dairy cows raised in the region, it is seen that 7.8 million tons of raw manure is produced annually, and about 600 thousand tons of manure will come from poultry farms in the region. No serious measures have been taken about the storage and disposal of manure; they are stored in an uncontrolled manner or used as raw fertilizer in agricultural areas and threating groundwater quality as a result of percolation in soil profile after precipitation and irrigation [41].

According to the reported total amount of inlet wastewaters to the treatment plants in the basin, approximately 20.5 thousand tons (dw) of sewage sludge per year is directed to anaerobic digesters [42],[43]. However, this annual sewage sludge generation in the basin is about 65 thousand tons (dw) when the population is considered [44],[45]. Therefore, the amount of sewage sludge that is needed to be handled properly each year is 44.5 thousand tons (dw) in the region.

Cattle and poultry manure were obtained from a regional farm and solar dried wastewater treatment plant (WWTP) sludge was collected from a municipal wastewater treatment plant in study region.

2.2 Experimental set up

The samples are homogenized, dried at 100°C and ground below 2 mm prior to the experiments. Approximately 10 g of sample was placed into the pyrolysis chamber at the room temperature and 10°C/min heating rate was applied under anaerobic conditions supplied with nitrogen flow. Three different final pyrolysis temperatures, namely; 350, 500 and 700 ^{o}C, were examined during the study. At the end of the experiment, after reaching the final temperature, the pyrolysis system was kept at this temperature for 30 min. The produced char was then collected from the system and used for the characterization studies.

2.3 Analytical procedures

The organic matter content of original samples was analyzed according to ASTM D2974-13 standard [46]. An IKA C200 bomb calorimeter was used for determining the calorific values of the samples. Volatile matter content analysis was conducted according to ASTM E872-82 and the ash content was determined according to ASTM E1755-01 [47],[48]. Fixed carbon is calculated according to Equation 1 [49]:

$$FC = 100 - M - VM - ASH \quad (1)$$

where FC is fixed carbon, M is moisture and VM is volatile matter. Since the samples were dried prior to the ash and VM analysis, the moisture in dry matter was taken as zero during calculations.

The elemental analysis (C, N, H) was conducted with Leco TruSpec CHNS (USA) according to ASTM D5373 standard and sulfur was measured regarding ASTM D4239 method [50],[51]. The oxygen content was calculated by difference. All analyses were carried out in triplicate and the mean values were presented.

Thermogravimetric analysis (TGA) has been applied by Perkin Elmer STA 6000 by using dry samples; the temperature increased from room temperature to 950°C at a rate of 10°C/min under nitrogen flow.

FT-IR analysis of the original samples (at room temperature) and produced biochars were conducted with Spectrum BX Perkin Elmer where the wavelength range was in between 4000 to 650 cm^{-1}, the resolution was 4 cm^{-1} and the number of scans was 25.

With the Brunauer, Emmett and Teller (BET) method, surface area measurements were made based on the nitrogen (N_2) gas adsorption technique in a liquid nitrogen environment at 77^{o}K. The degassing procedure took place at 250^{o}C for 4 h. Surface morphology of biochars was analyzed via scanning electron microscope (SEM) (Zeiss-Gemini560).

3 Results and discussion

3.1 The properties of waste samples

The proximate analysis results, water and organic matter contents and calorific values of original samples are given in Table 1. Cattle manure had the highest volatility of 83.44%$_{dw}$ and organic matter content of 83.91%$_{dw}$. On the other hand, sewage sludge was higher in ash content with 39.24%$_{dw}$. The highest calorific value was found in cattle manure as 5476 kcal/kg$_{dw}$ which was consistent with the volatile matter. Moreover, similar results were obtained with the literature values. In a study conducted in Thailand, the average volatile matter value and ash value for sewage sludge were found to be 42.4%$_{dw}$ and 53.2%$_{dw}$, respectively, and the maximum values were 60.2%$_{dw}$ for volatile matter while minimum value for ash is 38.4%$_{dw}$. The minimum and maximum fixed carbon values were found to be 1.8%$_{dw}$ and 11.8%$_{dw}$, respectively, while the maximum calorific value was reported as 3346 kcal/kg$_{dw}$ [52]. In a study conducted by Otero et al., volatile matter value for sewage sludge was measured between 50.8-59.3%$_{dw}$, ash value was between 30.8-43.3%$_{dw}$ and calorific value was between 3189-4009 kcal/kg$_{dw}$ [53]. The volatile matter value for cattle manure was reported as 64.66%$_{dw}$, while ash value was 14.66%$_{dw}$ and fixed carbon was 20.67%$_{dw}$ in the study of Cely et al. [54]. In the same study, volatile matter, fixed carbon, ash for poultry manure were found to be 64.85%$_{dw}$, 14.92%$_{dw}$ and 20.24%$_{dw}$ respectively [54]. In another study, volatile matter value for cattle manure was 69.51%$_{dw}$, ash value was 15.37%$_{dw}$, and fixed carbon was 15.12%$_{dw}$ [55]. Quirog et al. found the average organic matter content of poultry manure to be 67.37%$_{dw}$, ash value 33.65%$_{dw}$ and calorific value 3127 kcal/kg$_{dw}$ [56]. Font-Palma reviewed the calorific values of cattle manures and found averagely as 3227 kcal/kg$_{dw}$ [31]. The data obtained for sewage sludge and poultry manure in this study is similar with the measurements reported in the literature, where volatile matter and calorific value of cattle manure determined here was more than 20% higher than the reported values.

3.2 The results of ultimate analysis

The results of ultimate analysis conducted in unprocessed (original) waste materials are given in Table 2. The cattle manure had the highest carbon content of 44.85%$_{dw}$ which is compatible with its volatility and calorific value. The hydrogen content of the samples was in the range of 4.85 - 8.40%$_{dw}$. The nitrogen and oxygen content of samples changed from 4.85 to 6.13%$_{dw}$ and 40.12 to 61.33%$_{dw}$, respectively, where the sulfur content was between 0.17- 0.73 %$_{dw}$. In the study conducted by Thipkhunthod et al. carbon, hydrogen, nitrogen and sulfur values of sewage sludge were found to be 21.21%, 3.35%, 3.12% and 1.03%, respectively. The oxygen value they reported was 20.75% on average, which is different from the value found in this study; this may be because of their calculation is based on ash-free content [52]. Otero et al. found the carbon value of sewage sludge between 30.1-38.3%, hydrogen value between 4.12-5.20%, nitrogen value between 3.69-4.51% and sulfur value between 0.56-0.91% [53]. Carbon value was 41.13%, hydrogen value 5.89%, oxygen value 49.92%, nitrogen value 2.69% and sulfur value 0.37% for cattle manure [55]. Quirog et al. measured the average carbon, hydrogen, nitrogen and sulfur values of poultry manure as 36.2%, 4.6%, 5.9% and 0.11%, respectively [56]. Therefore, the results of the ultimate analysis are found in parallel with the values given in the literature.

Table 1. The initial properties of waste samples.

Sample Code	**Sample Type**	**Organic Matter Content, $\%_{dw}$**	**Volatile Matter, $\%_{dw}$**	**Ash, $\%_{dw}$**	**Fixed Carbon, $\%_{dw}$**	**Calorific Value, $kcal/kg_{dw}$**
CM	Cattle Manure	83.91	83.44	14.16	2.40	5476
PM	Poultry Manure	66.84	70.92	26.15	2.92	3355
SS	Sewage Sludge	50.22	58.48	39.24	2.28	3388
	Ref. [52]-[56]	62.8-71.5	42.4-69.51	14.66-53.2	1.8-20.67	3127-4009

Table 2. The results of ultimate analysis.

Sample Code	**C, $\%_{dw}$**	**H, $\%_{dw}$**	**N, $\%_{dw}$**	**S, $\%_{dw}$**	**O, $\%_{dw}$**
CM	44.85	8.40	6.13	0.50	40.12
PM	32.11	5.58	5.85	0.17	56.29
SS	28.24	4.85	4.85	0.73	61.33
Ref. [52]-[56]	21.21-41.13	3.35-5.89	2.69-5.9	0.11-1.03	20.75-49.92

3.3 Thermogravimetric analysis

The resulting graphs of the thermogravimetric analysis (TGA) and differential thermal analysis (DTA) for CM, PM and SS are presented in Figure 1. The main weight loss of all samples was observed between 200 and 500°C. According to the TGA curves, the weight loss in SS isn't much compared to others as expected, which is a result of its higher ash content describing the inert fraction of the material originated from treatment and conditioning chemicals used in the WWTPs. The DTA graphs show that, after the slight water losses around 100°C, combustion reactions are observed at 280°C in all samples. There are char formations at 450 and 600°C for SS, while it can be observed at 660 and 750°C for CM and there are some char formations around 600°C for PM. Previously, Zaker et al. found the main weight loss range for SS to be between 200-400°C [57]. In another study, according to the DTA graph, an exothermic reaction due to the combustion of carbons is observed around 300°C [58]. It was also reported that the main weight loss for CM and PM was between 200-550°C, where exothermic reactions were observed around 300°C in the DTA graphs and the char formations were seen at 550°C for CM and 650°C for PM [54].

3.4 The biochar yields of waste samples

The biochar yields of waste samples were calculated as a result of experiments because the amount of biochar is an important parameter to determine the process temperature. The results are given in Table 3. As expected, the least amount of biochar production was observed at 700 °C and the most at 350°C from all three samples. In other words, the amount of biochar decreases as the temperature increases. If high biochar production is preferred, lower temperatures should be used [5]. Among the three samples, the least amount of biochar was produced from the CM sample in accordance with the proximate and ultimate analyzes. The SS sample produced the most biochar due to its high inorganic content.

Table 3. The biochar yields of waste samples

	Biochar yield		
Temperature, °C	**350**	**500**	**700**
CM	52.07	30.09	22.56
PM	52.49	39.33	35.48
SS	63.64	52.74	37.79

3.5 The results of FT-IR

The FT-IR analysis was conducted to learn the functional groups, chemical structures and chemical constituents of samples and biochars obtained at temperatures 350, 500 and 700°C.

The spectra displayed several peaks specifying the complex structures of CM, PM, SS and their biochar samples. The major peaks can be seen in Figures 2- 4 showing different compounds and the type of bonds available in these fractions. It is expecting that O-H, CH and CH_2 bonds will remove, and C-O bonds will stay and form. The results were interpreted according to the literature.

According to the results, water loss occurred in SS before 350°C, because the O-H band, which can be seen at the wavelength of 3304-3280 cm^{-1}, disappears at this temperature [59]-[63]. The bands in the range of wavenumbers from 2924 to 2850 indicated that the presence of cellulose, hemi-cellulose and lignin. Moreover, C-H and C-H_2 bands (at 2924-2850 cm^{-1}) disappeared at 350°C in PM and SS. C-H band weakened at 350°C for CM and disappeared at 500°C [59],[62]-[64]. The loss of O-H stretching of hydroxyl groups and C-H stretching of aliphatic CH_x shows that the samples were subjected to dehydration and depolymerization [59]. Moreover, the disappear of these bands indicates the successful pyrolysis of the samples as we expected [59]-[64].

The 1649-1517 cm^{-1} stretch in the spectra was originated from C=C stretching of aromatic components [59],[60],[64]. C=C band was disappeared at 500°C in CM and PM, while it was disappeared at 350°C in SS. The transmittance spectrum of the samples and biochars, except biochars of CM at 500 and 700°C, presented distinct C-H band from deformation in cellulose and hemicellulose between 1466-1313 cm^{-1} [59],[61],[64].

C-O band caused by stretching vibration in cellulose and hemicelluloses can be observed at the wavelength of 1274-1014 cm^{-1} [59],[61],[62],[64]. The peaks in this interval were mostly become indistinct with increasing temperature. In another words, as the temperature increased, the structure of the biochars became more regular in this wavelength range [62].

The peaks at the wavelength of 877-666 cm^{-1} are due the aromatic rings [59],[62],[64]. Siengchum et.al. found that the predominance of the transmittance spectrum at the wavelength between 1480-700 cm^{-1} for the samples and biochars indicates that the samples consist of lignin. Moreover, they indicated that the existence of intense transmittance band between 1242-

1030 cm^{-1} for C-O stretching means that the samples also consist of cellulose [65]. Furthermore, Siengchum et.al. mentioned that the broad transmittance bands between 1745-1375 cm^{-1} for the samples and biochars indicates that they mainly contain lignin and cellulose [65], [66].

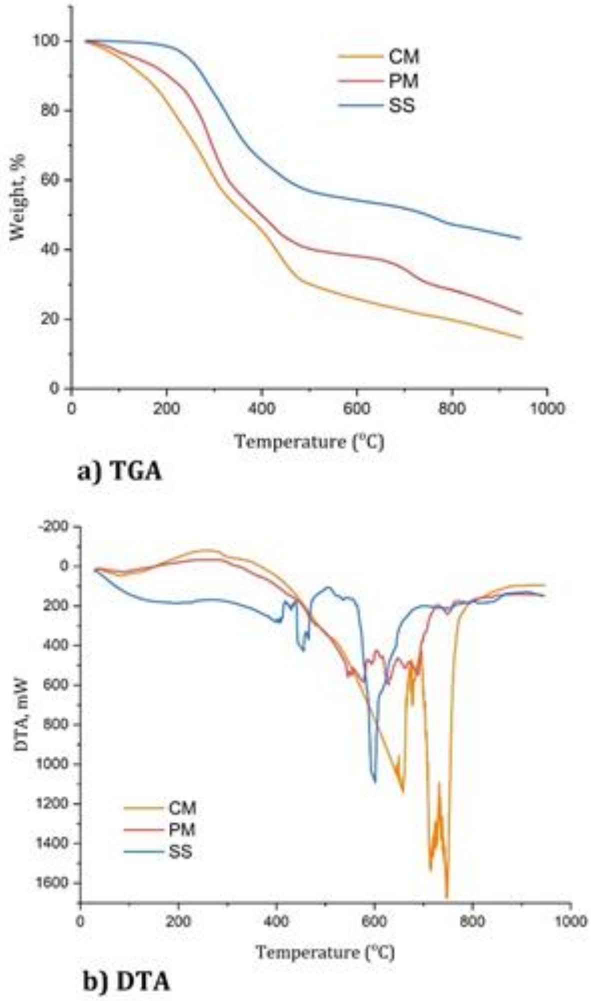

Figure 1. The TGA-DTA results of CM, PM & SS: a) TGA & b) DTA

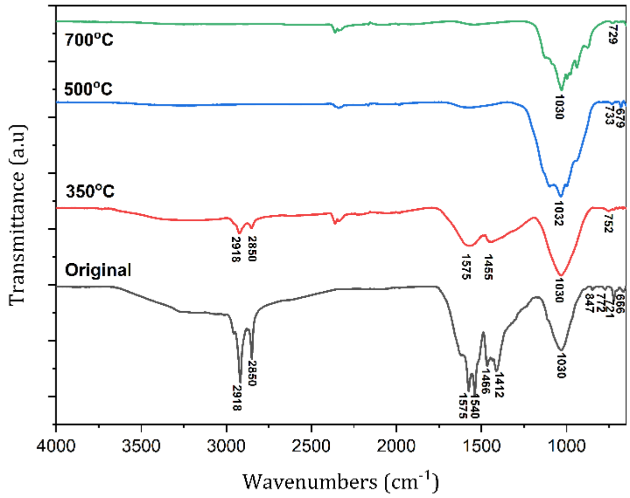

Figure 2. FT-IR results of CM

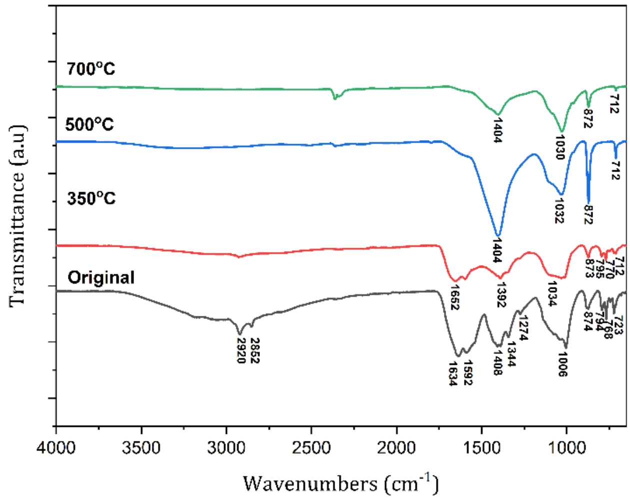

Figure 3. FT-IR results of PM

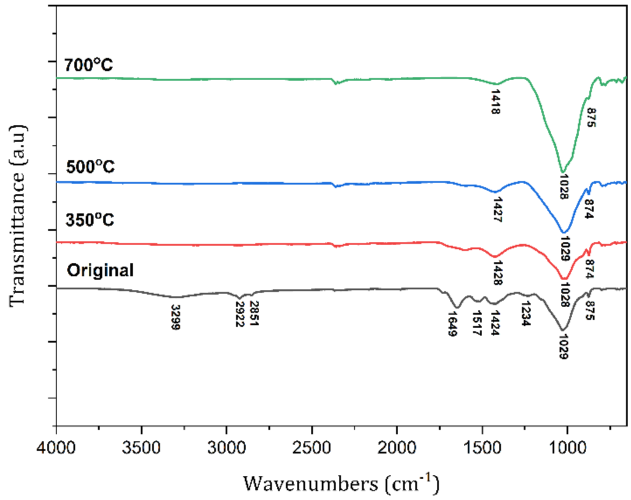

Figure 4. FT-IR results of SS

The FT-IR results show that the removal of O- and H-comprising functionalities in biochars is due to pyrolysis at higher temperature. The absence of these bands in biochars are important because it shows the formation of CO_2, CH_4 and H_2, due to the pyrolysis of cellulose, hemicelluloses and lignin [62]. Moreover, the FT-IR results point out that the biochars can be used in the production of the adsorbents for wastewater treatment because the soft-carbon components disappeared and hard-carbon components were preserved [64]. Intensity of bands mostly decreased with increasing temperature. On the other hand, the results stated that even at temperature of 700^{o}C, C-H, C-O bands and aromatic rings were preserved. This can prove the presence of pyranose rings and guaiacyl monomers of cellulose and hemicellulose [59].

3.6 The results of BET

The BET surface area and pore volume of biochar samples are given in Table 4. It can be seen that both the BET surface areas and pore volumes of biochars were significantly increased with temperature increase except SS whose BET surface area decreased at 700°C. Surface area increases because carbon mass leaves from the biomass as volatile matter, so pores are formed in the biochar [63]. Biochar of CM at 700°C has the highest BET surface area which is compatible with proximate and ultimate analysis. Although BET values vary widely in the literature, the results are consistent with these values and the effect of temperature is clearly seen. In their literature review, Singh et al. reported the BET values of biochar produced from SS in the range of 24.3-260 m^2/g and as the temperature increases, the BET surface area and pore volume increase [15]. In another study, they obtained biochar from SS and CM at 550°C. The BET surface areas of these biochars were found to be 14.033 m^2/g and 3.98 m^2/g, respectively [67]. These values were much lower than the values obtained in this study. Although the highest BET values of the biochar found in the study are lower than the illite BET values in the literature, they are higher than bentonite and kaolinite BET values, which are known as good absorbents [68].

Table 4. The results of BET

Sample Code	BET Surface Area, m^2/g	Pore Volume, cm^3/g
CM-350	1.6296	0.008
CM-500	22.9497	0.138
CM-700	47.5858	0.357
PM-350	7.8414	0.055
PM-500	9.7394	0.061
PM-700	11.3092	0.606
SS-350	1.9192	0.287
SS-500	41.7567	0.024
SS-700	21.2004	1.002

Although the BET values in this study are generally appropriate, they need to be improved. For this purpose, the BET value can be increased by using chemical activators and acid washing [69]. Zaker et al. produced biochar from SS and increased the BET value from 69.63 m^2/g to 899.33 m^2/g by subjecting the biochar to chemical treatment with NaOH and HCl [57]. In another study, biochar was obtained from PM. The BET surface area increased from 2.68 m^2/g to 5.79 m^2/g with the increase in pyrolysis temperature from 300°C to 600°C. Although these values are compatible with the values in this study, they do not show the same properties as the activated carbons on the market. The BET surface area of commercial activated carbons varies between 500 m^2/g and 1000 m^2/g. For this reason, additional chemical activation is needed [70]. In another study, CM was subjected to pyrolysis at higher temperatures and the BET surface area was found to be 170 m^2/g [71].

3.7 The results of SEM

The surface characteristics of biochar samples produced at 700°C are shown in Figure 5 and SEM images of biochars synthesized at 350°C and 500°C are given in the supplementary (Supplementary A). It can be seen that all samples have crack structures. Ma et. al. found similar structures for CM [71]. Moreover, the SEM images of SS and CM biochars obtained by Stylianou et al. at 550°C are similar to those in this study [67]. The increase in temperature enhanced the cracks and fragmentation in the structures of the biochars similar to that found by Zhang et al. [72]. Cuixia et al. supported this result with their study on biochar synthesized from PM [73]. In addition, characteristic structures were observed especially in the biochars synthesized from PM. On the other hand, when the SEM image of SS biochar obtained at 500°C is examined, it is understood that it has a more porous structure than the biochar produced at 700°C. While this result is consistent with the BET values; the reaction of the inorganic additives in the SS, that is melted at high temperatures, may have caused this result. SEM analysis shows that SS biochar synthesized at 700°C has a much less porous appearance than that produced at 500°C, supporting the hypothesis.

4 Conclusion

As a result of the study, it was observed that the yield of biochar produced decreased with the increase in temperature. According to the FT-IR results, the production of biochar from the wastes subject of the study was successful. The pores observed in the SEM figures along with the BET results support this result. The study reveals that biochar synthesized from cattle and poultry manure by pyrolysis at 700°C provides higher surface areas than those obtained at 350°C and 500°C. However, the surface area of sewage sludge biochar synthesized at 700°C was found to be smaller than that synthesized at 500°C. This is attributed to the higher inert content of the sludge; this fraction possibly melted at temperatures above 500°C and trapped part of the organic fraction that was converted into biochar. This finding suggests that not only the pyrolysis temperature plays a role in the quality of biochar, but also the mass fraction of the inorganic content of the feedstock and possibly the mineralogical structure of the inorganic fraction. The unit surface areas of the synthesized biochars are promising and indicate that further studies are needed to increase these surfaces by further processing. "These findings show that the production of biochar has the potential to significantly decrease the environmental impact associated with the production of manures and sewage sludge within the basin. Essentially, this means that waste materials, which represent significant carbon sources, can be effectively utilized by transforming them into alternative materials."

5 Acknowledgement

6 Author contribution statements

In the work carried out, both authors contributed to forming the idea and making the design of the pyrolysis experiments. Author 1 completed the literature review, sampling and sample preparation, performed the analysis and contributed to the examining the results. Author 2 contributed to the evaluation of results, conclusion and checking the article in terms of content.

7 Ethics committee approval and conflict of interest statement

"There is no need to obtain permission from the ethics committee for the article prepared."

"There is no conflict of interest with any person/institution in the article prepared."

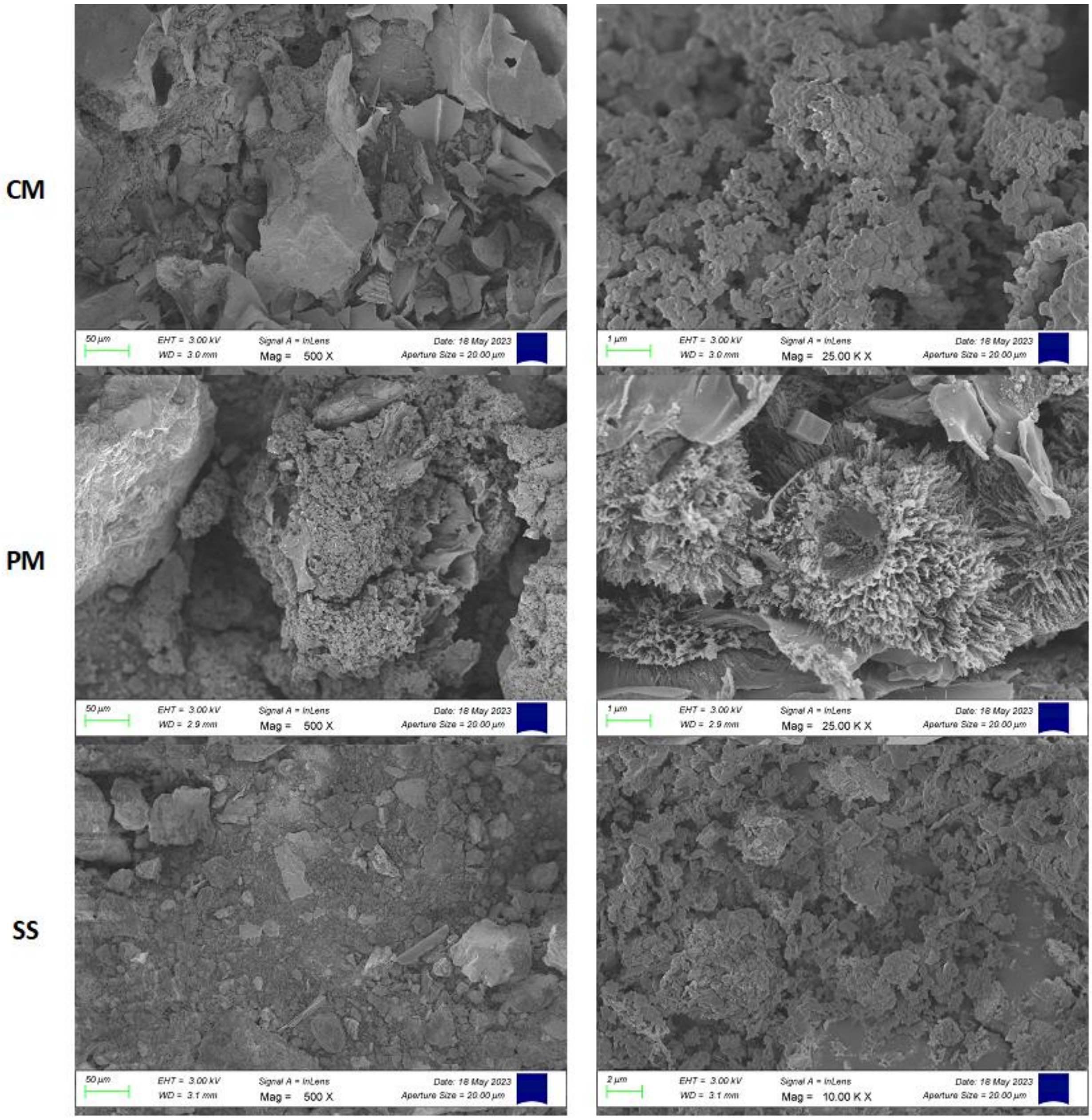

Figure 5. SEM images of CM, PM and SS at 700°C

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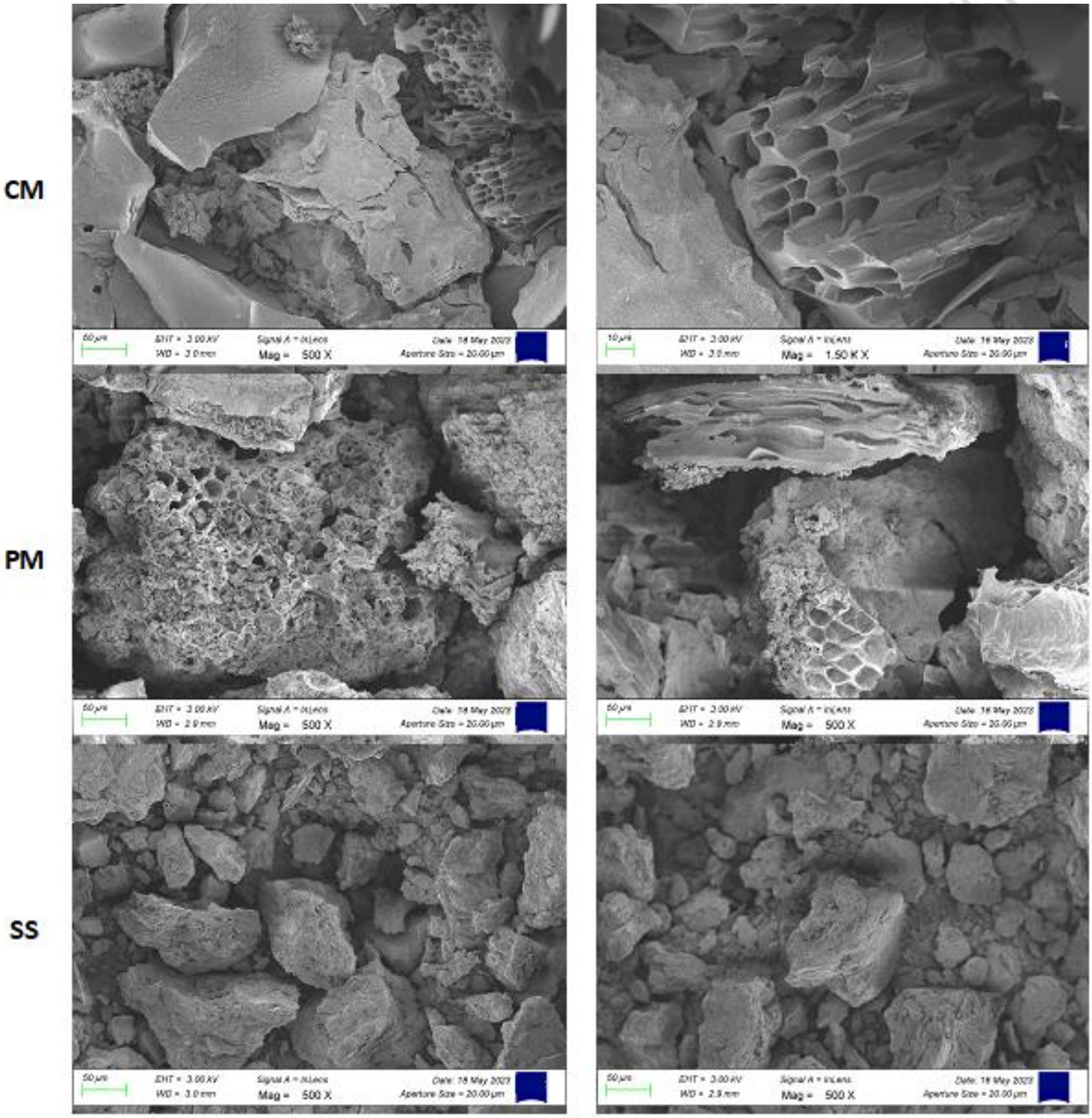
Supplementary A

SEM images of CM, PM and SS at 350°C:



SEM images of CM, PM and SS at 500°C: