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Utilization of Digestate from Agricultural and Food Waste for the Production of Biochar Used to Remove Methylene Blue

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Abstract: The treatment of waste or by-products from the agri-food industry in agricultural biogas plants results in the production of biogas. After anaerobic digestion, digestate remains and is often used for soil fertilization. The solid digestate (SD) can also be used for the production of biochar, a material with specific properties and many applications. Such a model of operation fits perfectly into the concept of a circular economy, because the waste material can be used to produce an adsorbent that can be used to treat industrial wastewater. The research assumption of this study was to investigate selected properties of biochar prepared at variable temperatures in the pyrolysis process from solid. The potential of biochar for methylene blue (MB) sorption was also initially investigated in terms of biochar's suitability for immobilizing metals in degraded soils. Biochar was produced at temperatures between 400–900 °C, with a temperature gradient of 50 °C. The efficiency of the production was in the range of 51–40% and decreased with the increasing temperature. The rising process temperature was also accompanied by a decrease in the nitrogen and hydrogen content of biochar. The produced biochar had an alkaline pH ranging from 11.40 to 12.69 and it increased as the temperature increased. The rise in the pyrolysis temperature effected a significant increase in the specific surface area BET (Brunauer–Emmett–Teller) in the case of biochar BSD_{750}, BSD_{800}, and BSD_{850} (BSD—biochar solid digestate). When analyzing the C content of individual biochar variants, there was no clear downward or upward trend, just as in the case of TOC (total organic carbon) value for the produced biochar. The greatest potential for removing MB (methylene blue) from solutions was demonstrated by biochar produced at 650–900 °C. The ability to remove MB rose along with the production temperature of the biochar.

Keywords: circular economy; methylene blue; properties of biochar; pyrolysis; solid digestate; sorption

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1. Introduction

The pursuit of the concept of a circular economy results in the use of various methods of transformation of waste or by-products from agri-food production [1] or municipal residues [2]. A circular economy refers to effective recycling by using the potential of waste and limiting its negative impact on the natural environment [3]. It is a very popular and economically justified process to convert various raw materials in biogas plants. This model not only allows the use of the organic matter and nutrients present in substrates, but also enables the production of heat and electricity from the produced biogas [4–6]. Combustion of waste from the municipal economy and agricultural production or even use in composting processes may involve potential climate changes as a result of greenhouse gas emissions. Currently, actions are being promoted to prevent climate change and to implement many innovations aimed at the proper use of environmental and public resources [7–9]. According to data published on the website of the Agricultural Property Agency [10], there are 120 agricultural biogas plants in Poland (as of 30 October 2020). The substrates that are converted in these biogas plants are most often waste and by-products from the agri-food industry. The most commonly used feedstocks are maize silage,

slurry [11] and residues from fruit and vegetables, and distillery stillage. It is estimated that between 15% and 40% of organic compounds contained in food waste are used to produce biogas, and the rest remains in the form of so-called digestate [12]. Solid digestate from anaerobic digestion of waste of plant or animal origin in accordance with Polish legislation is classified as waste [5]. However, research [13] indicates that solid digestate may be an ideal raw material for the production of sorbents used for industrial purposes. Appropriate valorization of this substrate is an important issue in the implementation of a circular economy. The properties of this product depend on the types of substrate used in the biogas plant [14–16] and the parameters of anaerobic biodegradation [17]. The digestate is characterized by the presence of a significant amount of organic matter, nitrogen, phosphorus, potassium, and micronutrients needed by the plant [11]. As it has been shown, the use of digestate as a biofertilizer can contribute to increasing yields by an average of 20% [18]. The use of digestate on arable land is, therefore, very justified, both in terms of fertilization and the economic aspect [11]. However, digestate is often associated with the problems of odor, pathogen content, and heavy metals (especially Zn and Cu). This may limit its use in soil as a biofertilizer. Importantly, the nutrients and heavy metals contained in digestate are characterized by high mobility, which means that they are easily washed out [19,20].

Moreover, the agricultural/fertilizer use of digestate may be limited due to the fact that in some countries there is already a developed market for the production of composts obtained from bio-waste or sewage sludge in biological stabilization [21]. However, a problem that often arises during the management of digestate is the need to manage large quantities of it, often resulting in the overfertilization of soils or the need to transport the produced product over greater distances. Therefore, it is desirable to seek and study actions that allow the exploitation of the potential uses of digestate [14,22].

A promising solution to the large quantity of digestate that is produced in biogas plants is the transformation of digestate into biochar. Biochar can be produced by various methods such as torrefaction, combustion, gasification, and slow and fast pyrolysis [11,17,23–25]. Among these processes, pyrolysis is a better option and an effective biochar production process [22–25].

Biochar is a material with specific properties. Its most important features include: high carbon content (50–90%), a well-developed specific surface, a porous structure and the presence of surface functional groups, a wide pH range (4–12), and low susceptibility to degradation and microbiological decomposition [26]. Important characteristics of biochar include its ability to undergo ion exchange and its degree of wettability. These properties determine its use in many processes, for example, in the composting process, soil improvement, metal retention in soil, and the removal of pollutants from water [27–47]. The specific properties of biochar mainly depend on the type of raw material and the temperature of the pyrolysis process [48–52]. The temperature of the process influences, among other things, the specific surface of biochar and the type of surface functional groups [39–41]. That is why it is so important to combine the choice of raw material, pyrolysis process temperature, heating time, and reaction time [29–54], to obtain the expected product with properties that allow it to achieve the desired effect. Due to the efficiency of the process, so-called slow pyrolysis is recommended for the production of biochar [55,56], during which metals are immobilized and phosphorus availability is increased [57–59].

As a natural fertilizer, biochar contributes to the transfer of organic matter and nutrients to the soil [32]. It can be used as a biosorbent [60–62] or for the sequestration of carbon in the soil [63].

The benefits of using biochar from digestate to improve soil properties result primarily from increased cation exchange capacity (CEC) and reduced purge of nutrients (mainly nitrogen and phosphorus) into groundwater [14]. Research shows that biochar prepared from solid digestate compared to biochar prepared directly from raw biomass has better properties in terms of improving pH and the adsorption effect [21,64,65]. According to [17], the characteristic features of biochar and digestate depend on the type of substrate used,

but also on the temperature conditions in the biogas plant. Tang et al. (2019) showed that biochar produced from fermented sewage sludge is a promising adsorbent and can be used to remove ammonium from urban wastewater [23]. Generally, biochar produced from solid digestate, due to its mesoporosity, abundance of nutrients, and functional groups, can be used as a potential biofertilizer, soil improver, or biosorbent [14]. Combining biochar with digestate for agricultural production also seems to be an interesting solution. An increase of up to 10% in yields was demonstrated when digestate with biochar was added to the crop. Additionally, biochar in this combination can act as an adsorbent and passivator for removing contaminants from fertilized soil. This seems to be a beneficial solution to the strategy of environmental reclamation and utilization of part of the generated digestate [21,64].

An analysis of the properties of biochar produced from solid residues from the anaerobic digestion of waste or by-products from agri-food production can be helpful in planning the process of their transformation. The analysis can used in waste management processes [66]. This applies not only to the planning phase of the construction of biogas plants but also to the concept of technical solutions related to the final transformation of solid digestate. It can be helpful in identifying potential uses of produced biochar, e.g., in soil improvement processes, increasing composting efficiency [67], or the sorption of organic or inorganic pollutants [63]. In addition, the need for sorbents to remove heavy metals from water [32], soil [68,69] or wastewater can be satisfied by biosorbents [70] produced from digestate. As emphasized by [71], the continuation and development of research on the use of biochar to remove nitrogen and phosphorus from wastewater or other media is currently very desirable. Panwar et al. (2019) draw attention to the importance of biochar in the processes of carbon sequestration and improvement of soil properties [47]. Many researchers indicate the need to develop research on the conditions of biochar production and its application in metal retention [33,72], because the raw material and the production method used have an impact on the adsorption properties of biochar [61,73]. Others indicate that the use of the solid digestate produced in the process of anaerobic fermentation of agricultural waste for the production of biochars may be used in the treatment of post-production wastewater containing dyes [74,75]. Sawalha et al. (2022) and Lu et al. (2022) indicate the need to activate or modify such biochars in order to increase their sorption capacity [76,77].

This type of digestate recycling meets the requirement of a bioeconomy and promotes the transition to a circular economy. The above measures are consistent with the UN Sustainable Development Goals (Goal 12.5—reducing waste generation and Goal 11.6—mitigating the impact on the environment during waste management) [17,20,22–25]. By processing digestate into biochar, greenhouse gas emissions are reduced, which is an important element of a sustainable circular economy. Figure 1 presents the traditional/conventional approach to the use of digestate and an innovative solution related to the production of biochar and its use in environmental protection.

The concept of using digestate in two ways—firstly as a fertilizer and secondly as a substrate for biochar production—seems to be an interesting strategy for its utilization. This strategy fits into the idea of a circular economy. This research was aimed at creating and characterizing the properties of biochar prepared from digestate under various temperature conditions. The methylene blue sorption experiment also allowed for a preliminary assessment of the ability of the resulting biochar to sorb heavy metal cations. Removing ubiquitous heavy metal ions from water and soil environments is still one of the greatest global challenges. Therefore, new methods are still being sought, and those already used are being modified, which will allow the removal of heavy metals from the natural environment. The use of biochar from digestate for this purpose seems to be an effective and environmentally friendly strategy [62].

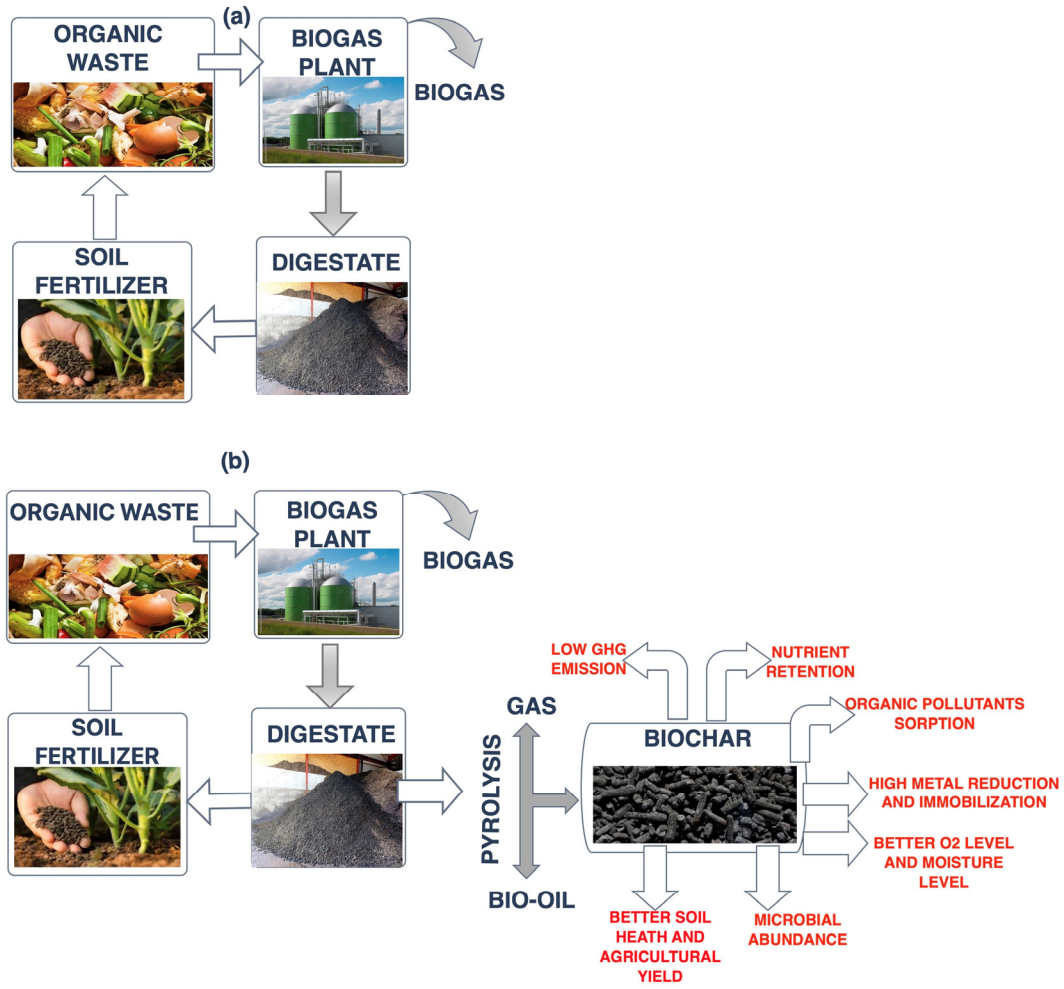

Figure 1. Circular economy mode with a conventional (**a**) and innovative (**b**) approach to digestate [21,26,27].

2. Materials and Methods

2.1. Substrates for Biochar Production

Solid digestate from the anaerobic digestion (SD) process at an agricultural biogas plant was used for the production of biochar. The biogas plant is located in central Poland and works with a capacity of over 8.000 MWh. This biogas plant uses animal manure, straw, and various types of waste from agri-food processing.

The moisture content (MC), ash content, pH, Kjeldahl nitrogen content (N_K), and total carbon (TC) were determined for the substrate (Table 1). A comparable ash content in the digestate was determined by Wiśniewski et al. (2015) in their studies. This value was equal to 26.62%. Similarly, in the case of total carbon, the authors of publication [24] determined the content of this parameter at the level of 39.68%.

Table 1. Selected properties of substrate (SD) for biochar production.

pH_{H2O}	MC	Ash	TC	N_K
		%		
8.45 ± 0.06	9.38 ± 0.27	26.08 ± 2.16	37.98 ± 0.40	1.99 ± 0.03

Table 2 shows the results of the content of cellulose, lignin, and hemicellulose in the substrate.

Table 2. Cellulose, lignin, and hemicellulose content in the substrate.

Extraction Substances	Cellulose	Lignin	Hemicellulose
	%		
4.12 ± 0.12	30.57 ± 0.67	38.72 ± 0.53	55.50 ± 31

2.2. Characteristics of the Pyrolysis Process

Solid digestate was subjected to the pyrolysis process in a PRW-S100x780/11 oven (Czylok Company, Jastrzębie Zdrój, Poland). The process was carried out in an atmosphere of inert gas—nitrogen, at a flow rate of 5 L·min^{-1}. The following pyrolysis temperatures were used: 400 °C, 450 °C, 500 °C, 550 °C, 600 °C, 650 °C, 700 °C, 750 °C, 800 °C, 850 °C, and 900 °C. The heating time to the target temperature was 120 min for temperatures 400–550 °C, 150 min for temperatures 600–750 °C and 180 min for temperatures 800–900 °C, respectively. The reaction time was 60 min. After the process was completed, the material was left in the reactor to cool. The produced biochar samples were placed in tight containers.

2.3. Physicochemical and Physical Analyses

The moisture content in the substrate (SD) and the obtained biochars (BSD) was determined by the drying–weighing method at a temperature of 105 ± 2 °C. The ash content was determined in accordance with PN-EN ISO 18122:2016-01—Polish version, Solid biofuels—Determination of ash content [78]. The total carbon content in solid digestate was determined in a Multi N/C analyzer (Analytkjena, Jena, Germany) in accordance with the standard PN-ISO 10694:2002—Soil quality—Determination of organic carbon content and total carbon content after dry combustion (elemental analysis) [79]. The Kjeldahl nitrogen content was determined in accordance with PN-EN 16169:2012—Polish standard. Sewage sludge, treated bio-waste and soil. Determination of nitrogen by the Kjeldahl method [80]. The pH measurement consisted of pouring 5 g of the sample with 50 mL of distilled water (in three separate beakers). The beakers were placed on a shaker and filtered after 10 min, after which the pH was measured (pH meter Cole Parmer Model No. 59002-00, Cambridgeshire, UK).

The substrate SD was analyzed for cellulose, lignin, and 1% NaOH soluble substances content. The test sample was ground in a mortar and passed through a sieve. The analyses were carried out on a sample containing particles with a particle size of 0.5 to 1.0 mm. The content of ethanol soluble substances (in Soxhlet) was determined, along with the content of substances soluble in 1% aqueous sodium hydroxide solution (1% NaOH), the cellulose content using the Seifert method, and the Klason lignin content using the TAPPI method (TAPPI T 222 om-02). The results are shown as an average of three determinations.

For the produced biochars, an elemental analysis of CHNS (carbon, hydrogen, nitrogen, sulfur) was performed using the Thermo Scientific™ (Madrid, Spain) FLASH 2000 dynamic combustion method. The total organic carbon content was determined in a Shimadzu TOC-5000A analyzer with the SSM 5000 attachment. The TOC analysis method was used, consisting of combustion at high temperature (900 °C), and carbon dioxide was measured by infrared spectrometry and expressed as carbon. The specific surface area of BET was analyzed on an ASAP 2420 device (Micromeritics). This analyzer measures single- and multi-point specific surface areas and the size and distribution of solid pore samples. Scanning electron microscopy (SEM) was used to determine the morphology of biochars. Surface functional groups were identified by Fourier transform infrared spectroscopy, which is frustrated total internal reflection (FTIR).

2.4. Methylene Blue Sorption

Solutions of methylene blue with initial concentrations (C_1) of 50 mgL^{-1}, 100 mgL^{-1}, and 200 mgL^{-1} were prepared. The produced biochars were crushed in a mortar and sieved (500 µm sieve). Weighted amounts of 0.4 g were prepared from the material, which were mixed with 20 mL of each of the prepared BM solutions at different concentrations. The

mixtures were prepared in three repetitions. The samples thus prepared were shaken on the laboratory shaker for 24 h, then left under static conditions for another 24 h. The final concentration of BM (C_2) in the solution was measured using a UV–VIS spectrophotometer (DR 500 HACH Lange) at a wavelength of 664 nm.

The percentage of MB removal was calculated according to the following formula:

$$W = \frac{C_1 - C_2}{C_1} \cdot 100\% \quad (1)$$

where:

C_1—initial concentration methylene blue mgL^{-1}

C_2—concentration methylene blue during balance mgL^{-1}.

2.5. Statistical Analysis

Statistical analyses were carried out using IBM SPSS Statistics 26 to verify the effect of biochar production temperature on the percentage of MB removal from solutions. It was used to perform basic descriptive statistics with the Shapiro–Wilk test, Spearman's rank correlation test, and single-factor variance analysis. The level of significance in this chapter is $\alpha = 0.05$.

3. Results and Discussion

3.1. Pyrolysis Process Yield

The efficiency of the pyrolysis process in the temperatures between 400 °C and 900 °C ranged from 51.09 ± 0.67% to 40.66 ± 0.23% (Table 3) and was much higher than that achieved by Stefaniuk and Oleszczuk (2015)—45.27–27.16%, when producing biochar from digestate [17]. This shows that the efficiency of the biochar production process depends on the type of substrate used. The highest yield of BSD biochar was observed at the lowest temperature, as in the studies by Shariff et al. (2016) [81]. As others indicate [55,81], the efficiency of biochar production is higher with a high content of lignin in the processed raw material. The high lignin content in SD makes it a desirable precursor for the production of biochar. According to [65], lignin-rich biomass allows for greater efficiency in biochar production, with a higher share of stable C (with process implementation at temperatures of 300 and 400 °C). The corresponding content of cellulose, lignin, and hemicellulose in SD does not require the addition of e.g., waste wood biomass during biochar production [65]. A fairly high ash content of about 26% was determined in the SD. Llorach-Massana et al. (2017) carried out analyses to determine the efficiency of the production of biochar from residues from tomato cultivation. Production capacity was 45% for the process at 350 °C, and 38% for the process carried out at 400 °C, respectively [73]. In research, producing biochar from SD (rich in lignin, cellulose, and hemicellulose) at 400 °C resulted in a much higher yield of about 51%. The efficiency of biochar production is also influenced by the ash content, usually higher in manure or sewage sludge [82], and lower in raw materials of plant origin [55]. In the SD used in the production of BSD biochar, the ash content was at a fairly high level (Table 1). An increase in the temperature of biochar production decreased production efficiency, as observed in other studies [17,23,48,83]. One reason for the decrease is, among others, the loss of volatile substances and the decomposition of cellulose, hemicellulose, and lignin present in the SD.

Table 3. Efficiency of biochar production at the adopted pyrolysis temperatures and their determined properties.

Type of Biochar	Yield	pH_{H2O}	MC	Ash	N	C	H	S	TOC	H/C	BET
	%		%	% dm							$m^2 \cdot g^{-1}$
BSD_{400}	51.09 ± 0.67	11.40 ± 0.56	0.51 ± 0.27	39.74 ± 1.20	2.14 ± 0.03	44.53 ± 0.09	3.13 ± 0.02	0.45 ± 0.04	44.1 ± 8.20	0.84	4.62 ± 0.19
BSD_{450}	47.95 ± 1.87	11.30 ± 0.20	2.51 ± 0.10	44.04 ± 3.00	2.02 ± 0.11	43.56 ± 1.35	2.42 ± 0.13	0.85 ± 0.007	45.0 ± 11.7	0.67	9.43 ± 0.32
BSD_{500}	46.76 ± 1.33	11.58 ± 0.33	0.62 ± 0.20	44.50 ± 1.86	1.98 ± 0.005	49.95 ± 0.62	2.33 ± 0.05	0.46 ± 0.03	46.7± 8.90	0.56	5.07 ± 0.23
BSD_{550}	45.56 ± 1.29	12.06 ± 0.62	0.61 ± 0.02	53.57 ± 2.05	1.72 ± 0.005	45.20 ± 0.68	1.68 ± 0.07	0.49 ± 0.01	44.1 ± 11.5	0.44	9.66 ± 0.43
BSD_{600}	45.30 ± 2.66	12.28 ± 0.42	0.37 ± 0.09	49.74 ± 3.56	1.79 ± 0.04	46.21 ± 0.35	1.44 ± 0.03	1.60 ± 0.19	42.5 ± 11.0	0.37	6.39 ± 0.25
BSD_{650}	43.49 ± 0.29	12.50 ± 0.25	0.72 ± 0.17	53.12 ± 3.03	1.73 ± 0.03	52.19 ± 1.16	1.28 ± 0.005	0.60 ± 0.005	48.5 ± 9.40	0.29	4.98 ± 0.68
BSD_{700}	41.96 ± 0.65	12.53 ± 0.24	0.42 ± 0.15	53.32 ± 3.51	1.64 ± 0.01	48.20 ± 0.95	1.12 ± 0.005	1.00 ± 0.02	45.0 ± 11.7	0.28	8.58 ± 0.44
BSD_{750}	41.29 ± 0.35	12.64 ± 0.31	0.94 ± 0.28	54.40 ± 1.20	1.44 ± 0.06	46.43 ± 1.32	0.97 ± 0.02	1.02 ± 0.05	45.2 ± 8.70	0.25	11.68 ± 0.38
BSD_{800}	40.71 ± 0.10	12.65 ± 0.09	0.69 ± 0.29	51.50 ± 1.34	1.22 ± 0.11	45.50 ± 1.22	0.82 ± 0.13	1.46 ± 0.08	45.0 ± 11.0	0.22	21.09 ± 0.43
BSD_{850}	40.63 ± 0.24	12.63 ± 0.39	0.65 ± 0.21	57.43 ± 6.94	1.62 ± 0.01	48.13 ± 0.02	0.65 ± 0.03	1.63 ± 0.03	44.4 ± 9,50	0.16	47.90 ± 0.35
BSD_{900}	40.66 ± 0.23	12.69 ± 0.18	0.97 ± 0.04	55.76 ± 1.91	1.01 ± 0.01	42.39 ± 0.52	0.68 ± 0.04	1.65 ± 0.27	35.9 ± 9.30	0.19	20.39 ± 0.12

3.2. Physicochemical Characteristics of the Produced Biochar

The results of the physicochemical analysis of the substrates are shown in Table 3.

The produced biochar had an alkaline pH between 11.40 ± 0.56 and 12.69 ± 0.18. Stefaniuk and Oleszczuk (2015) described a similar pH range for biochar made from digestate [17]. The pH values of BSD biochar are significantly higher than those indicated for biochar produced at similar temperatures from other substrates [84]. For example, the pH of biochar produced by [72] from poultry litter at 560 °C was equal to 8, and had a significantly lower value than the pH of BSD_{550}. Similarly, in the case of biochar produced at 500 °C from poultry manure tested by [83], the pH value was 10.5. When analyzing the pH value of BSD biochar, a trend was observed of an increase in this value with the increase in temperature of the pyrolysis process, also observed by other researchers [83]. This trend is due, among other things, to an increase in ash content and carbonate formation.

The moisture content of the analyzed biochar did not exceed 1%, except in one case for which the moisture content was equal to 2.52%. This was probably due to a leak in the container where the biochar samples were stored.

The ash content of biochar ranged from 39.74 ± 1.20 to 57.43 ± 6.94%. The highest value was determined for BSD_{900}. A slightly lower ash content in the range of 14.12–43.56% was obtained in the study of biochar from digestate by [17]. The ash content of BSD biochar was lower than that of biochar produced from sewage sludge [82], but higher than in the case of biochar made from substrates of plant origin, which had a lower ash content [39,85]. In their research, Zielińska et al. (2015) determined the maximum ash content of biochar from sewage sludge at 79% [82]. However, in biochar from poultry manure (i.e., also of fecal origin) produced at 600 °C, [86] determined the ash content at a lower level of about 49.90%. Similar ash content was determined for biochar BSD_{600} (49.74%). As indicated by [86], the ash content of biochar can affect its sorption of organic impurities. That has been confirmed by the research of [39]. Analysis of the ash content of BSD biochar has generally shown an upward trend with the increasing pyrolysis temperature. This effect is probably triggered by the increasing number of inorganic components and the residues of the combustion of organic matter [84].

The results of the elementary analysis of biochar showed an N content between 1.01 ± 0.01% and 2.14 ± 0.03%. Pyrolysis carried out at a higher temperature resulted in a reduction in the nitrogen content in biochars, as observed by other researchers [17,48,82,85]. The decrease in N content was probably due to the loss of nitrogen compounds with an easily degradable structure. The hydrogen content of the analyzed biochar ranged from 0.68 ± 0.04% to 3.13 ± 0.02%. As the pyrolysis temperature increased, a decrease in the hydrogen content in biochars was also observed, probably caused by dehydration and loss of H atoms. A similar phenomenon was also observed by [17,48,82]. The determined C content of biochar ranged from 42.39 ± 0.52%to 52.19 ± 1.16%. No clear downward or upward trend was observed when analyzing the C content of individual biochar variants. Similarly, it was observed in studies by [57] in which the C content of biochar produced from biosolids (at temperatures of 450, 600, and 750 °C) did not differ significantly. The results presented by [31] indicate an increase in C content as the temperature of the biochar production process increases. In studies, the C content of biochar produced at the highest temperature was determined at the lowest level. As Srinivasan et al. (2015) demonstrated by studying biochar of different origins produced at 680 °C, the C content of plant biochar was significantly higher than in biochar based on excrement [63]. Similar observations were made by [85]. The C content of BSD_{650} was determined at approximately 52%, which is significantly lower than the results presented by [63]. The sulfur content of the produced biochar varied greatly. The smallest content (0.45 ± 0.04%) was determined in biochar produced at 400 °C, while the highest (1.65 ± 0.27%) was in BSD_{900} biochar. However, there were no clear upward or downward trends between these extreme values.

The TOC content of all biochar variants, except BSD_{900}, exceeded 40%. The highest TOC content (48.5 ± 9.40%) was determined for BSD_{650} and the lowest (35.9 ± 9.3%) for

BSD_{900}. In comparison, the TOC content for hardwood biochar (pyrolysis temperature 580 °C) in studies by [87] was at the level of 52.3% and for BSD_{550} the content was set at 44.1 ± 11.5%. However, taking into consideration the requirements of the European Biochar Certificate [88] for the organic carbon content of biochar used in agriculture, the organic carbon content should be >50% d.m. The low organic carbon content in analyzed biochar variants does not, however, exclude their other applications.

The value of the calculated H/C molar ratio of biochar showed a pronounced downward trend with the increase in temperature, as in the studies by Li and Chen (2018). The reduction of H/C indicates the increasing aromaticity of biochar [86,89]. Changes in the C and H content of biochar produced at different temperatures determine the value of the H/C ratio, which should not be greater than 0.7 as required by the [88]. This value has been exceeded only for BSD_{400} biochar. However, for BSD_{800} and BSD_{900}, the H/C ratio was close to 0.2, which may point to the transformation of aromatic structures into graphite structures [48]. Biochar produced at 800 and 900 °C can show the potential for long-term carbon sequestration when added to the soil [48].

The analysis of BET-specific surface values did not show a strongly developed specific surface area. The BET values were between 4.62 ± 0.19% and 47.90 ± 0.35%. For BSD_{400}, BSD_{500}, BSD_{600}, and BSD_{700} biochar, the BET value did not exceed 10 $m^2 \cdot g^{-1}$ and varied for individual biochar variants, without the clear upward trends presented in other studies [24,69,70]. The increase of the BET-specific surface values from 11.68 ± 0.38 $m^2 \cdot g^{-1}$ to 21.09 ± 0.43 $m^2 \cdot g^{-1}$ happened with an increase in the temperature of biochar production from 750 °C to 800 °C. This increase in BET surface was made even more apparent for BSD_{850}—the value of BET was then 47.90 ± 0.35 $m^2 \cdot g^{-1}$. With a further increase in the biochar production temperature to 900 °C, the BET value decreased to 20.39 ± 0.12 $m^2 \cdot g^{-1}$. Hung et al. (2017) [14] and [89,90] observed similar dependencies. Biochar studied by these authors, obtained at 800 °C, had a significantly increased BET area (approx. 101.9 m^2/g) compared to biochar produced at 700 °C (6 m^2/g), which the authors explain by a combination of high aromaticity and mineral calcination, and mesoporous structure [14]. As the pyrolysis temperature increased, the specific area of biochar increased, probably due to the decomposition of cellulose and hemicellulose and the formation of a channel structure [39]. Raw material with a high lignin content has the potential to produce biochar with a large surface area and porosity [31]. Therefore, high values of the specific surface are usually characteristic of biochars from plant biomass, while biochars from manure usually have smaller specific areas [86]. However, a higher ash content can block the growth of the specific surface area and total porosity due to inhibition of the development of micropores when creating mesopores [86]. These factors may have influenced the development of the specific surface area of BSD biochar.

Figure 2 shows the microstructure of the selected BSD biochar variants. The most porous structure is that of BSD_{850}, which confirms the determined value of the specific area.

The potential for the use of biochar in the process of sorption of various pollutants from the environment is determined by, among other things, the type of functional groups present on its surface [91]. Therefore, biochar produced from SD was subjected to ATR–FTIR (Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy) analysis to observe differences between products produced at different temperatures. The biochar selected for analysis included BSD_{400}, BSD_{500}, BSD_{600}, BSD_{700}, BSD_{800}, and BSD_{900}. The results of the analysis are shown in Figure 3. Biochar produced at higher temperatures was characterized by fewer surface functional groups.

The FITR analysis of the studied biochar showed the presence of vibrations stretching the O–H bonds in BSD_{400} and BSD_{500} biochar, in the area ~3351–3173 cm^{-1}. For biochar BSD_{600}, BSD_{700}, BSD_{800}, BSD_{900} such vibrations were not found, which indicates the breakdown of volatile OH groups, loss of volatile substances and water, at temperatures of 600, 700, 800, 900 °C.

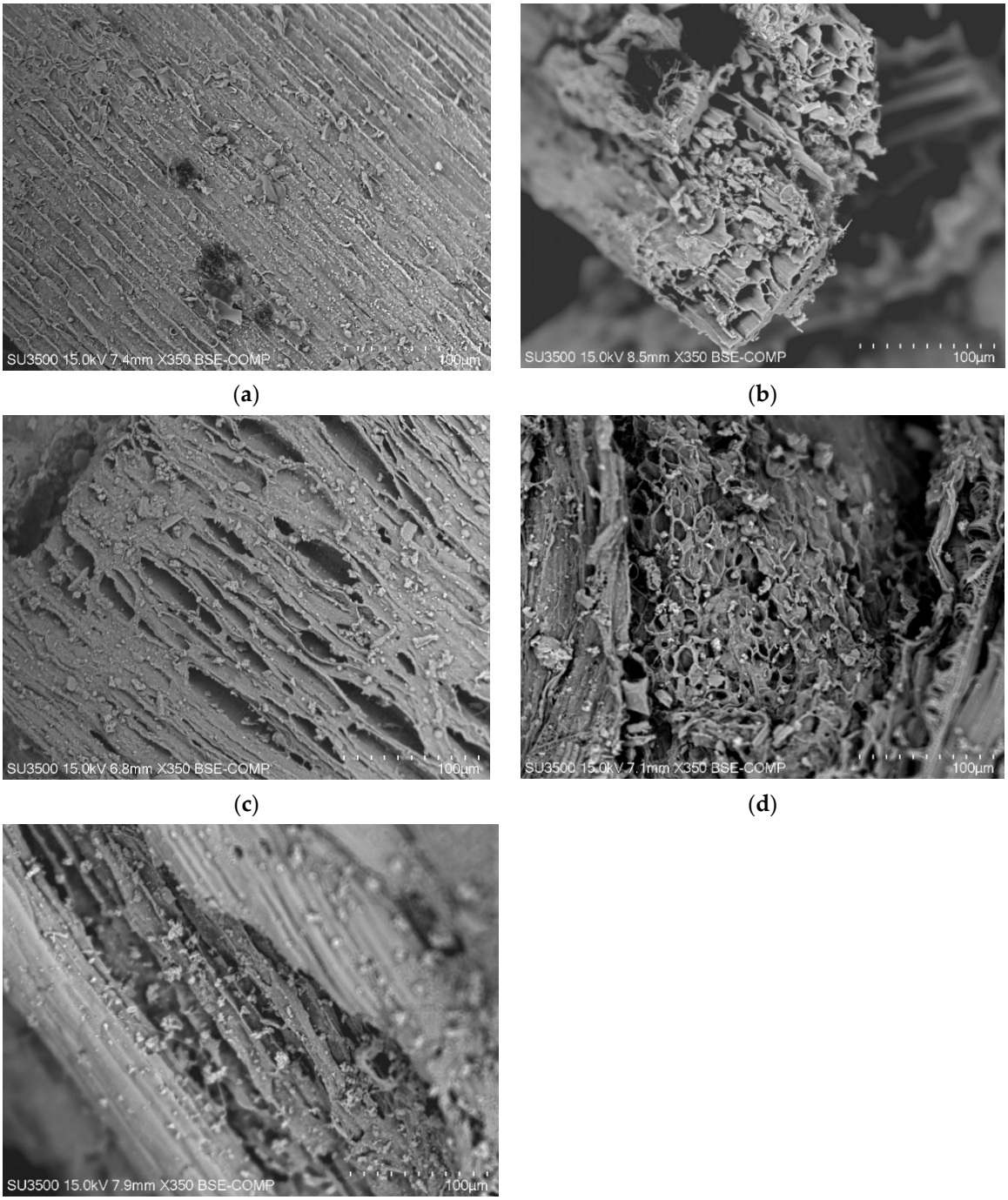

Figure 2. Microstructure of biochar: (**a**) produced at a temperature of 400 °C (BSD_{400}); (**b**) produced at a temperature of 450 °C (BSD_{450}); (**c**) produced at a temperature of 750 °C (BSD_{750}); (**d**) produced at a temperature of 850 °C (BSD_{850}); (**e**) produced at a temperature of 900 °C (BSD_{900}).

A signal assigned to the deformation modes of C–H groups, occurring in the area of 1470–1397 cm^{-1}, was observed by the FTIR spectra analysis of all tested biochar variants (in the area 1408–1400 cm^{-1}). The intensity of the peaks corresponding to these vibrations decreased with the increase in the temperature of biochar production, which may indicate the transformation of organic matter (lignin, cellulose, hemicellulose) and the release of volatile substances [83].

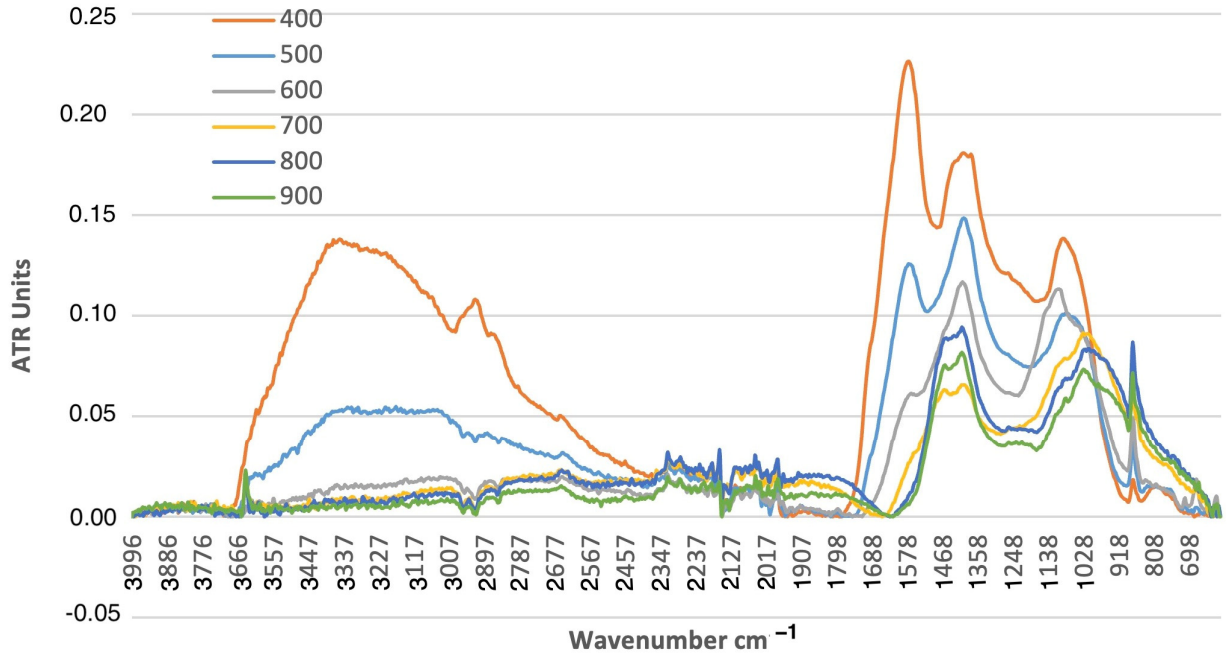

Figure 3. FTIR/ATR spectra of biochar produced at different temperatures (400 °C, 500 °C, 600 °C, 700 °C, 800 °C, and 900 °C) from SD.

Only in the case of BSD_{400} biochar, the analysis revealed the presence of a group of bands assigned to the C–H bond stretching modes (in the area ~2929 cm^{-1}), present in aliphatic compounds. The absence of such vibrations in the FTIR spectra of other biochar variants may indicate the transformation of the groups in question into aromatic structures [48] and a reduction in the biochar capacity for sorption of nutrients resulting from the presence of acidic functional groups [50].

In the FTIR spectra of biochar BSD_{400} and BSD_{500}, for wavelengths of 1575 cm^{-1} and 1572 cm^{-1}, respectively, vibrations stretching the C=C bonds were determined. The absence of clear signals corresponding to these vibrations in the spectra of other biochar variations may be caused by the breakdown of multiple double C=C bonds at ≥600 °C and a decrease in the number of structures with C=C bonds in the biochar [48].

C–O bonds stretching vibrations were observed on the FTIR spectra of all tested biochar variants in the range ~1104–1010 cm^{-1}. The presence of such signals may indicate the formation of aromatic ethers as a result of the inclusion of oxygen atoms in cyclic carbon structures [92]. The presence of C–O groups can compensate for the low specific surface area of biochar and positively affect its sorption properties [63]. The presence of oxygen-containing functional groups on the surface of the biochar is very desirable, mainly in terms of the use of biochar for metal immobilization. These groups are important in the creation of organometallic compounds that immobilize heavy metals in the soil (Pb (II), Cu (II), Ni (II), and Cd (II)) [92–94].

An analysis of the FTIR spectra of all tested biochar variants showed the presence of vibrations bending the =C–H bonds, in the range ~874–817 cm^{-1}, which may indicate the presence of polycyclic aromatic structures [29].

3.3. Methylene Blue Sorption Studies

The biochar dose used helped to achieve the level of removal of MB from the solution for all biochar variants above 80% (Figure 4). Franciski et al. (2018), in their studies using activated biochar (with a specific surface area of 80 m^2g^{-1}) at a dose of 1 gL^{-1}, achieved an MB removal level of 70% [40]. Hasnan et al. (2018), by studying the sorption capacity of biochar, obtained a percentage of MB removal from the solution equal to 99.45% [95]. They used unmodified biochar, having a large specific surface area equal to approximately

200 m^2 g^{-1} at a dose of 10 gL^{-1}, but with a lower concentration of MB in a solution of 10 ppm. By using the BSD_{400} and BSD_{450} biochar, approximately 97% of MB removal from the 50 mgL^{-1} solution was achieved. For higher concentrations of 100 mgL^{-1} and 200 mgL^{-1}, the effects achieved by using the biochar variants listed were poorer. Tang et al. (2019) showed that biochar produced at 450 °C from fermented sewage sludge is a promising adsorbent and can be used to remove ammonium from urban wastewater. The sorption potential of this biochar was probably due not only to the specific surface, but also to the presence of specific functional groups [23].

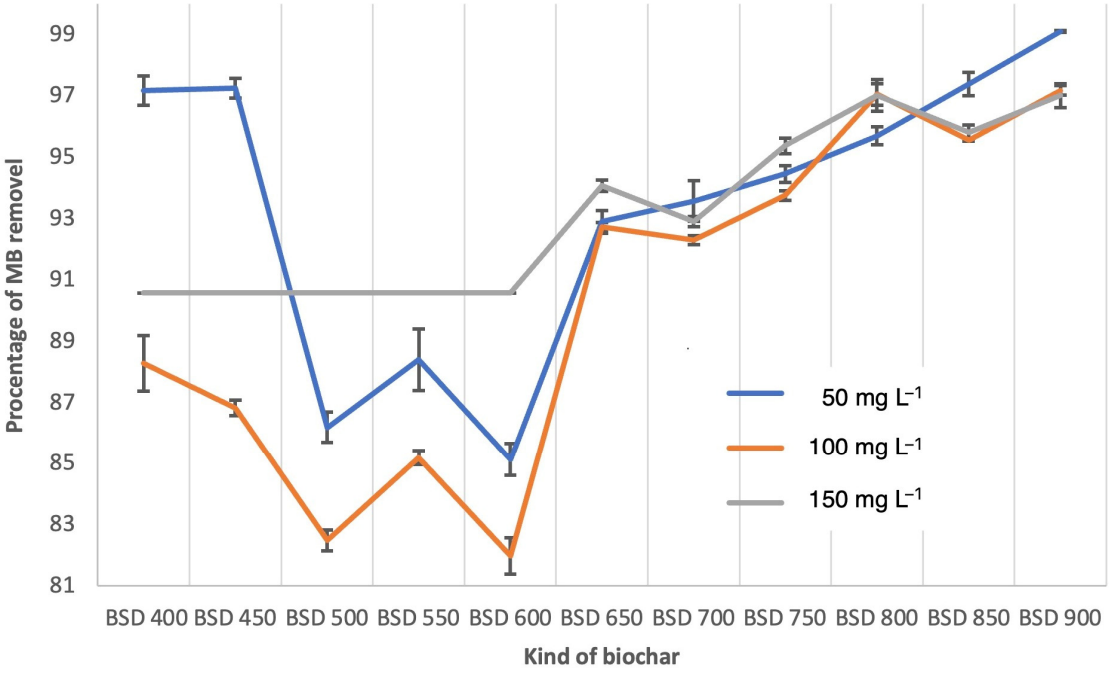

Figure 4. Percentage of MB removal from solution for biochar produced at various temperatures.

The poorest effects in removing MB from all three solutions were achieved using biochar BSD_{500}, BSD_{550}, and BSD_{600}. The effect of removing MB from a solution with a concentration of 200 $mgL^{-1)}$ for BSD_{400}, BSD_{450}, BSD_{500}, BSD_{550}, and $BSD_{600,}$ was at <91%. Using biochar BSD_{650}, BSD_{700}, BSD_{750}, BSD_{800}, BSD_{850}, and BSD_{900} demonstrated significantly better MB removal. This is confirmed by studies of [81], who established the usefulness of biochar produced at temperatures of 600–900 °C in the adsorption of heavy metals. MB as a cationic dye is a good indicator of the ability to remove heavy metal cations [55]. In addition, by analyzing the results obtained for BSD_{650}, BSD_{700}, BSD_{750}, BSD_{800}, BSD_{850}, and BSD_{900}, there was a trend of an increase in the percentage of MB removal from solutions using biochar produced at increasingly higher temperatures. A maximum removal value of MB of 99% was obtained for the BSD_{900} biochar.

As demonstrated by [60] in the mechanism of MB sorption on biochar, an important role is performed by the complexing of the surface in which functional groups -OH, -COOH, -CO, and -CH participate. In our experiment, the presence of -OH groups found in BSD_{400} and BSD_{500} may have had a positive effect on MB sorption. The absence of vibrations stretching the -CH bonds found for biochar produced at $\geq$ 500 °C may result in a decrease in the sorption capacity of biochar produced at these temperatures. The increase in sorption capacity for BSD_{800}, BSD_{850}, and BSD_{900} may be due to a larger specific surface area determined for the biochar variants listed compared to the others. The highest specific surface value determined for BSD_{850} did not translate into a maximum removal value of MB from the solution for this biochar. The relatively high percentage of MB removal for all biochar variants with a relatively low specific surface area may be due to the behavior of

C–O groups, which compensate for the low specific surface area of biochar and positively affect its sorption properties.

In the initial stage of the statistical analysis, the distributions of the quantitative variable of the percentage of methylene blue removal were checked. For this purpose, basic descriptive statistics were calculated together with the Shapiro–Wilk test, which examines the normality of the distribution. The Shapiro–Wilk test was statistically significant (Table 4). This means that the distribution of the test variable differs significantly from the normal distribution. It should be noted, however, that the skewness does not exceed the conventional absolute value of 2, so the distribution is asymmetric to a negligible extent [96]. Therefore, if the other assumptions were met, parametric tests were performed.

Table 4. Basic descriptive statistics of the tested variables together with the Shapiro-Wilk test.

	M	**Me**	**SD**	**Sk**	**Kurt**	**Min**	**Maks**	**W**	***p***
Percentage of MB removal	92.30	92.99	4.59	−0.66	−0.48	81.41	99.13	0.93	<0.001

M—average, Me—median, SD—standard deviation, Sk—skewness, Kurt—kurtosis, Min—the smallest value of distribution, Maks—the largest value of distribution, W—Shapiro–Wilk test statistics, *p*—significance.

An analysis of the Spearman's rank correlation was carried out to investigate the relationship between the temperature of biochar production and the percentage of methylene blue removal. The calculations were carried out on the basis of individual concentration values as well as for all the samples tested together. Analysis of the Spearman's rank correlation, without division based on the concentrations of solutions, between temperature and percentage of methylene blue removal, was statistically significant, positive, and strong. This means that a higher biochar production temperature coexists with a higher percentage of methylene blue removal from the solution. Spearman's rank correlation analysis, taking into consideration the types of concentrations of solutions, revealed statistically significant positive and very strong relationships between temperature and methylene blue removal percentages from solutions with concentrations of 100 mgL^{-1} and 200 mgL^{-1}. The analysis did not reveal a relationship between the variables in the case of a solution with a concentration of 50 mgL^{-1}. This result means that a higher biochar production temperature is coexisting with a higher percentage of methyl blue removal in the group of solutions with the concentrations of 100 and 200 mgL^{-1}, but this relationship does not occur for a group of solutions with a concentration of 50 mgL^{-1}. The results of the analyses carried out are presented in Table 5.

Table 5. The connection between the temperature of biochar production and the percentage of removal of methylene blue.

Temperature—Types of MB Concentration	***rho* Spearmana** / **Significance**	**Percentage of MB Removal**
Temperature—all types of MB concentration	*rho* Spearmana	0.64
	significance	<0.001
Temperature—concentration 50 mgL^{-1}	*rho* Spearmana	0.33
	significance	0.063
Temperature—concentration 100 mgL^{-1}	*rho* Spearmana	0.80
	significance	<0.001
Temperature—concentration 200 mgL^{-1}	*rho* Spearmana	0.92
	significance	<0.001

Using a single-factor variance analysis, it was verified whether the percentage of methylene blue removal was statistically significantly differentiated in terms of solution concentrations. The result of the ANOVA was statistically significant, and the force of the effect was revealed as weak (Table 6). The post hoc test was statistically significant in two pairs of variables, between 100 mgL^{-1} and 50 mgL^{-1} and 100 mgL^{-1} and 200 mgL^{-1};

the analysis did not show a statistically significant difference between 50 mgL^{-1} and 200 mgL^{-1}. The percentage of removal of methylene blue from the solution was higher at 50 mgL^{-1} and 200 mgL^{-1} compared to the concentration of 100 mgL^{-1} (Figure 5). However, no differences were observed between 50 mgL^{-1} and 200 mgL^{-1}.

Table 6. Results of a single-factor analysis of variance testing the percentage differences in methylene blue removal in terms of solution concentration.

MB Concentration	M	SD	F	*p*	η^2
50 mgL^{-1}	93.40	4.65			
100 mgL^{-1}	90.31	5.44	5.07	0.008	0.10
200 mgL^{-1}	93.20	2.67			

M—average; SD—standard deviation; F—the result of the analysis of variance; *p*—significance; η^2—effect size.

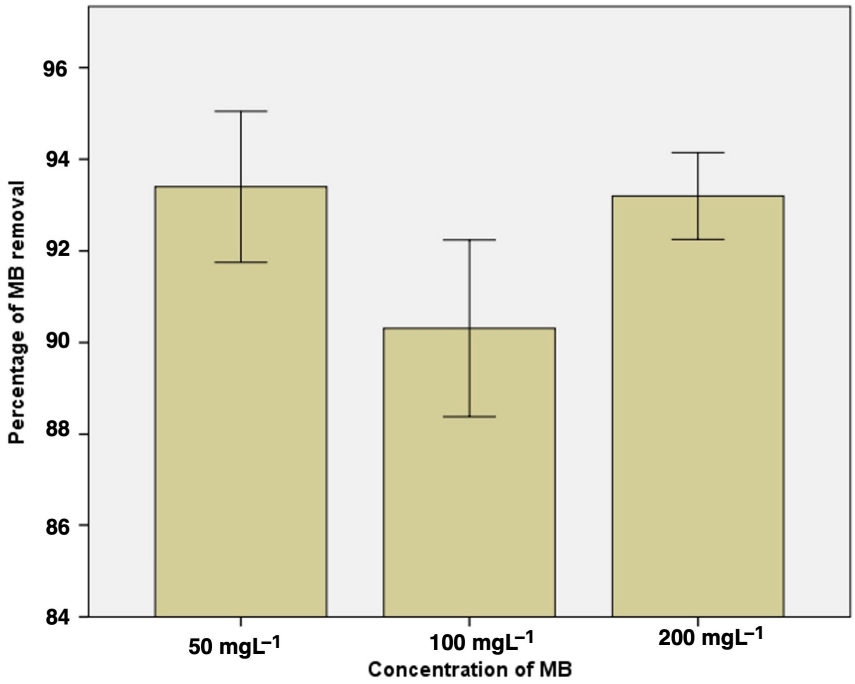

Figure 5. The average percentage of methylene blue removal in relation to the concentration of the solution.

4. Conclusions

The processing of solid digestate in the pyrolysis process has allowed the production of biochar with different properties. Process temperature is a very important factor influencing the yield of biochar produced from SD, its quality, and the ability to remove MB. The increase in pyrolysis temperature has resulted in a decrease in the efficiency of biochar production (from 51.09 ± 0.67%—400 °C to 40.66 ± 0.23%—900 °C) The rising process temperature was also accompanied by a decrease in the N and H content of biochar. Similarly, the H/C of biochar showed a pronounced downward trend with increasing temperatures. The opposite trend was observed for the pH (11.40 ± 0.56—400 °C and 12.69 ± 0.18—900 °C) and ash content of biochar (from 39.74 ± 1.20—400 °C to 57.43 ± 6.94%—900 °C). The value of these parameters increased as the temperature increased. In the case of the BET-specific surface, the increase in pyrolysis temperature resulted in a pronounced increase in the value of this parameter for biochar BSD_{750}, BSD_{800}, and BSD_{850}. When analyzing the C content of individual biochar variants, there was no clear downward or upward trend; the TOC value was behaving similarly for the produced biochar. BSD biochar produced at higher temperatures was characterized by fewer surface functional groups. It was noticed that for biochar produced at higher temperatures (>650 °C) there was an increase in the

degree of MB removal from aqueous solutions. A maximum MB removal value of 99% was obtained for the BSD900 biochar. The conducted analysis of biochar produced from solid digestate indicated that it can be used to improve the properties of soil, especially acidic soil due to its high alkalinity. The aromaticity of biochar, increasing with the rising pyrolysis temperature, demonstrates its usefulness in the sequestration of carbon in soil. Biochar produced at lower pyrolysis temperatures (<650 °C) can be successfully used as an effective soil additive aimed at limiting the leaching of nutrients from it. Due to the presence of many surface functional groups, it can also be used to remove ammonium nitrogen from wastewater. The capacity for removal of methylene blue from solutions indicates the possibility of using biochar from solid digestate in the process of heavy metal sorption, and therefore for the remediation of land contaminated with heavy metals. The studies demonstrated the high sorption potential of prepared biochar. In the future, there are plans to use a number of additional chemical and physical treatments leading to modification of the properties of biochar and expanding the scope of its use. The research results may help in making decisions regarding the creation of new enterprises integrating biogas plants and sewage treatment plants with plants processing digestate or sewage treatment waste (sewage sludge). This approach to waste management, which results in the production of products with added value, fits very well into the idea of a circular economy.

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