The effects of using biochar to remove ammonium nitrogen generated during the processing of biodegradable waste

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A B S T R A C T

The article described the attempt to use biochar as a sorbent to reduce the ammonia formed while composting a mixture of kitchen waste with chicken droppings and straw, and ammonium nitrogen from the leachate generated in this process. Two types of biochar were used, differing in the substrate used and the preparation temperature. The first biochar was prepared from beech wood chips (BBCh) at 600°C and the second from sewage sludge (BSS) at 500°C. The composting process was carried out for 10 d due to the largest ammonia emission that occurs at the initial stage of the composting process. It was found that the reduction of ammonia on the biochar prepared from sewage sludge was on average 17% lower compared to BBCh. The degree of ammonia reduction ranged from 54% (day 2) to 74.9% (day 10). The effluent formed during composting was treated under static conditions using both types of biochar. Their doses were changed in the range from 0.5 to 4.0 g dm^{-3}. It was found that the sorption process with 10% higher efficiency, on average, took place on the biochar prepared from chips (BBCh). The rate of ammoniacal nitrogen removal for BBCh ranged from 17% (0.5 g dm^{-3}) to 34% (4 g dm^{-3}) and for BSS from 14% (0.5 g dm^{-3}) to 24% (4 g dm^{-3}). BBCh biochar is characterized by a greater sorption potential concerning both the removal of ammonia from gaseous products and ammonium nitrogen from leachate. Achieving better sorption effects is probably conditioned by a change in the surface chemistry of biochar in the modification process, and even their activation (especially in the case of BSS biochar).

Keywords: Biochar; Composting; Gas ammonia; Ammonium nitrogen; Sewage sludge; Beech chips

1. Introduction

Biochar is a product that has been the focus of many researchers in recent years. This is mainly due to the wide range of potential applications resulting from its specific properties. The research is on the use of biochar as an additive to improve soil properties [1–5], reducing the bioavailability of pollutants [6], plant growth and crop yield [3,5], and heavy metal mobility [2,7–9], and their accumulation in plant biomass [10] is being carried out. The impact of biochar on the composting process [11–15] and emissions of greenhouse gases or odors [16–18], is also widely analyzed. The use of biochar as a sorbent of impurities from various media is also being investigated [19–22]. The use and positive effect of biochar depend on its properties [23], which in turn result primarily from the type of substrate used for production and the technical parameters of the pyrolysis process used [2,4,23–26]. Biochar is characterized by specific properties that predispose them to specific applications. The sorption properties of biochar are influenced

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by the type of raw material (elemental composition, lignocellulosic compositions) and the technical conditions of the pyrolysis process [18,27]. Properties such as high specific surface area, biochar porosity, high ion exchange capacity, and thermal stability are determined by the sorption properties [28]. The sorption possibilities of biochar are an issue studied by many authors, both with regard to the inorganic and organic substances [18,27,29,30]. Biochar can be used for the sorption of pollutants, including those from aqueous solutions [22,30–33]. The possibility of sorption of various ingredients on biochar makes them potential nutrient carriers, very desirable and attractive in terms of the environmental applications [28,32,34,35]. The biochar produced at lower and higher temperatures can be good sorbents because the high temperature of the biochar production process is not always correlated with high adsorption capacity [28,32,34]. Although increasing the process temperature affects the specific surface area and porosity. By properly implementing the pyrolysis process, biochar sorbents can be produced for various applications with specific sorption potential for organic and inorganic impurities, and their attractiveness can be effectively increased by modification in the chemical or physical processes as well as the creation of composites with other raw materials [21,28,29,33,36,37]. Biochar produced from various substrates (modified or unmodified) were tested for the sorption of nitrogen or its compounds [32,34,37,38]. The use of sorbents made from waste materials may be a more economical process due to the high cost of commercial sorbents [19]. Therefore, the production of biochar from residues from agricultural production or waste generated in the municipal sector, which is still a significant problem for waste management personnel in the aspect of choosing the method of their management, seems to be a good solution. This approach will not only prevent the negative impact of waste on the environment but will allow it to produce goods with added value, which perfectly fits into the circular economy model.

Sewage sludge can be one of the substrates for biochar production. The use of thermal processes for transforming sewage sludge allows recovering the energy contained in the sludge [12], but also acquiring new products with added value [39], which can be included in the environment enabling to recover carbon, nitrogen, and phosphorus, among others. Sewage sludge can be a good raw material for the production of adsorbents (effectively removing, e.g., dyes and metal ions) in carbonization processes, and the use of physical and chemical activation [21,39,40]. The changes in the pyrolysis and activation conditions have a direct impact on the adsorbent properties, adsorption capacity, and the mechanism of removal of impurities by sediment-based adsorbents [37]. Tang et al. [32] showed that the biochar produced from digested sewage sludge is a promising adsorbent for ammonium removal from municipal wastewater. The biochar produced at 450°C had the highest adsorption capacity, probably due to its larger surface area and the presence of functional groups [32] and the sorption mechanism is probably monolayer chemical adsorption. The possibility of using the biochar from sewage sludge for the recovery of ammonium in urine has also been demonstrated by Bai et al. [35], who used such enriched biochar

for soil conditioning. The biochar characterized by a high Mg content can be a valuable sorbent of NH_4^+–N and the phosphorus from aqueous solutions, with the nature of the substrate from which biochar is made, is important [28]. As reported by Baber et al. [41], the biochar sorbents can be used as an effective soil improver. The biochar fertilizer produced in this way can be used to improve soil properties or for the bioremediation of degraded areas. As research shows [42], such slow-release fertilizers used on sandy soils are more effective than mineral fertilizers. The possibility of using the biochar from sewage sludge for the recovery of ammonium in urine was demonstrated by Bai et al. [35], who used such enriched biochar for soil conditioning.

The use of biochar during composting can be realized not only by adding to the composted mixture but also as a sorbent of the possible odors (NH_3) produced in this process. Biological stabilization of waste carried out in the composting process, especially those rich in nitrogen (chicken manure, sewage sludge) not only results in obtaining a valuable product – compost – but is also associated with the emission of ammonia [11,43,44]. The ammonia emissions during the composting of organic municipal waste fractions range from 18 to 150 gNH_3 Mg^{-1} waste [45]. The use of biochar as a filter fill can effectively reduce the odor nuisance of this process. The authors [46] suggest that biochar is a promising alternative sorbent for removing gaseous volatile organic compounds.

The article proposes the use of biochar as a sorbent to reduce the odor emissions (NH_3) accompanying this process [47,48] and to remove ammonium nitrogen from the leachate generated during this process. The use of biochar for the recovery of ammonium nitrogen from leachate can positively affect the functioning of the technological system of the treatment plant, but also creates the possibility of obtaining a product, that is, a nitrogen-enriched sorbent. The aim of the study was to show whether the biochar prepared from sewage sludge is an effective sorbent for the removal of gaseous ammonia from post-process gases generated during composting and ammonium nitrogen from effluents.

2. Materials and methods

2.1. Biochar

Two types of biochar were used in the study, differing in physicochemical properties. The first biochar was prepared from natural beech wood chips (BBCh) in a pyrolysis process carried out in a tube furnace. The pyrolysis process was carried out at a temperature of 600°C. The produced biochar had a specific surface area of 300 m^2 g^{-1}, pH = 6.5. The total carbon content was determined at 85%. The nitrogen content was not determined. The second biochar was produced from municipal sewage sludge (BSS) by pyrolysis at 500°C. The biochar from sewage sludge was characterized by a much smaller specific surface area of approximately 40 m^2 g^{-1}. The carbon content was about 26%, the nitrogen content was 2.4%, and the pH was determined at 8.12. Table 1 summarizes the parameters of the biochar used and in Fig. 1 presents their photos along with a picture of their microstructure.

Table 1
Biochar parameters used in the study

Type of biochar	BBCh	BSS
Pyrolysis temperature, °C	600	500
pH	6.80	8.12
N, %	—	2.4
C, %	85.03	25.99
BET, $m^2 g^{-1}$	305.27	49.55

BIOCHAR FROM BEECH CHIPS
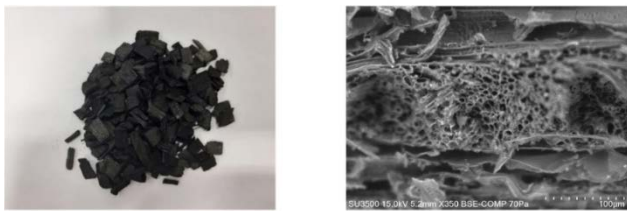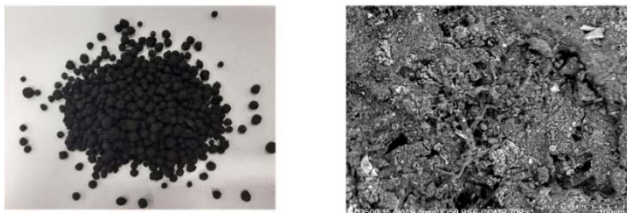

BIOCHAR FROM SEWAGE SLUDGE

Fig. 1. Biochar used in research prepared with beech chips and sewage sludge.

2.2. Composting process

The tests were carried out simultaneously in two bioreactors. Each bioreactor had a capacity of 45 dm³ and was equipped with a suction-pressure pump maintaining an adequate degree of aeration (maximum up to 60 dm³ h⁻¹), a temperature monitoring system, and process gas removal. The bioreactors were made entirely of stainless steel. In their upper part, the removable covers allow for easy loading of the charge and sampling of the material at any time. The air was supplied from the bottom of the reactors and its flow was controlled using a flow rate regulator (at this stage of the test the airflow was set at 30–33 dm³ h⁻¹). In the lower part of the reactors, there is a double perforated plate allowing air to flow through the bed of material. The temperature measurement in the bioreactors was conducted by three sensors located at 10 cm intervals from the double perforated plate. One of the bioreactors (B1) was additionally equipped with a filtration column with a biochar charge (500 g) located in front of the Dreschl scrubber. The filtration column is made of organic plexiglass (capacity – 10 dm³, diameter – 25 cm, and height – 29 cm). The post-process gas from the bioreactor was introduced at the bottom of the filter and the purified gas was collected at the top of the biofilter and then directed to a Dreschl scrubber. The gas purification efficiency (η) on the used biochar was calculated according to the following relationship [49]:

$$\eta = \left(1 - \frac{C_{eff}}{C_{inf}}\right) \times 100\%$$

(1)

where C_{eff} is the concentration of pollutant in the purified gases, mg dm⁻³; C_{inf} is the concentration of the pollutant in the inlet gases, mg dm⁻³.

The post-process gases from the second bioreactor were directed to a Dreschl scrubber (filled with 1 M H_2SO_4) in which the ammonia produced was adsorbed. The scheme of the test setup is presented in Fig. 2.

The research was divided into three stages (Fig. 3):

• ammonia removal from the post-process gases on the BBCh biochar (composting in the B2 + reactor in the B1 reactor with a filter column filled with the BBCh biochar),
• ammonia removal from the post-process gases on the BBS biochar (composting in the B2 + reactor B1 reactor with a filter column filled with BBS biochar),

1 – pump, 2 – rotameter, 3 – bioreactor, 4 – temperature control system 5 – Dreschl washer filled with 0,1M H₂SO₄,
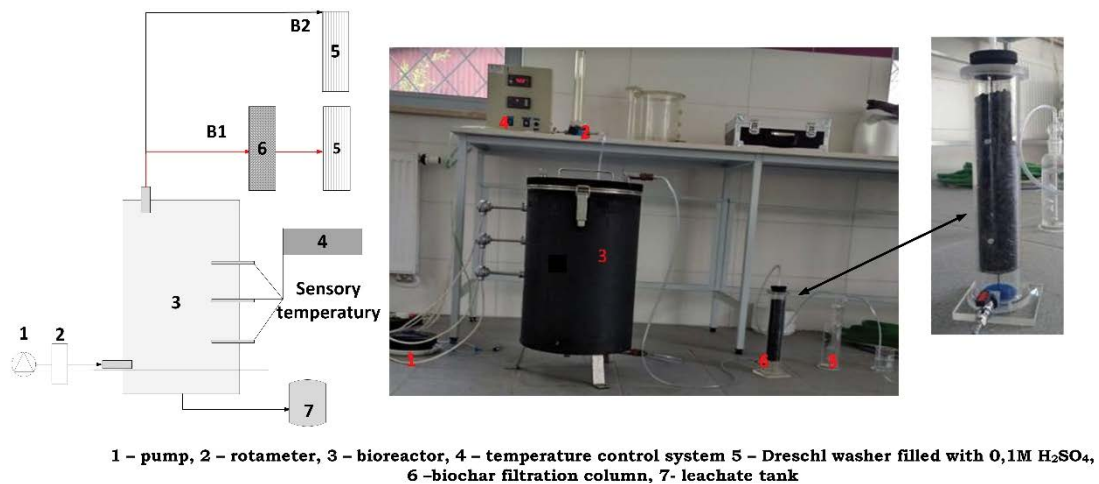6 –biochar filtration column, 7- leachate tank

Fig. 2. Setup for conducting the biochar treatment process of gases generated in the composting process.
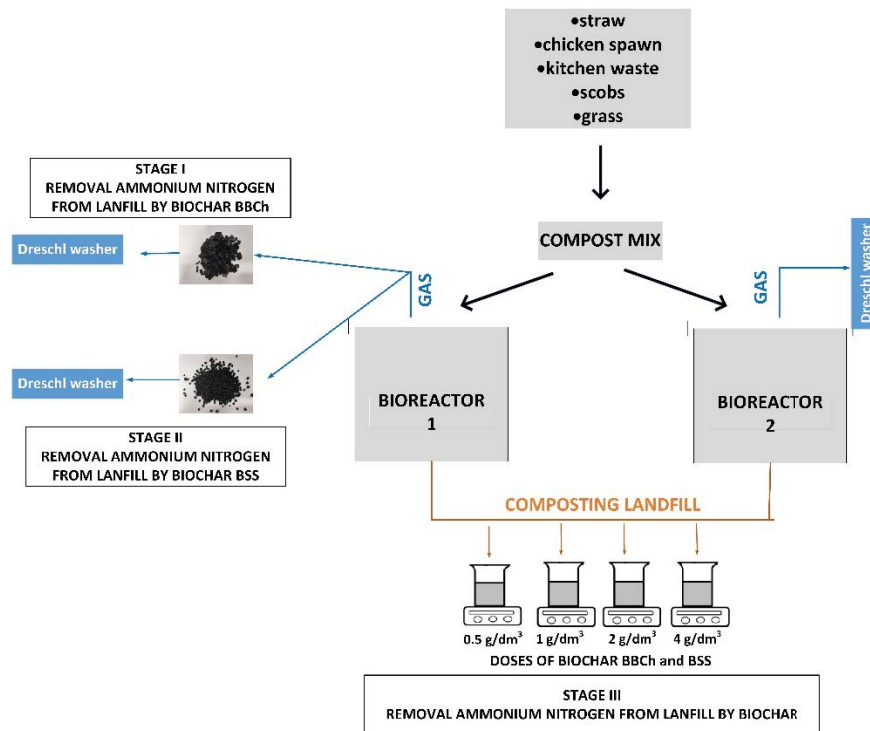
Fig. 3. Schematic diagram of the conducted research.

- use of BBCh and BBS biochar to remove the ammonium nitrogen from the leachates generated during composting.

The composting process in stages 1 and 2 was carried out for 10 d due to the largest ammonia emission that occurs at the initial stage of the composting process. Kitchen waste (5%), chicken manure (5%), straw (20%), grass (30%), and sawdust (10%) were used as substrates for the compost mixtures. For easier mixing of the substrate, water was added to the mix (30%).

The proportions of the mix (input for bioreactors) were determined based on the parameters of the substrates. Table 3 presents the average values of inputs (compost mixes) used in stages 1 and 2.

2.3. Adsorption of ammonium nitrogen on biochar

Adsorption of ammonium nitrogen from the leachate generated during composting was carried out under static conditions for the samples with a volume of 100 cm³. The doses of BBCh and BBS biochar were varied from 0.5 to 4 g dm⁻³. These biochar samples were shaken for 6 h and next they were left for 18 h of static contact. The mixing intensity was set at 150 rpm. The effectiveness of the adsorption process at the assumed doses and contact times was assessed based on the amount of ammonium nitrogen removal and the sorption capacity of the studied biochar was calculated from the following relationship (2):

$$q = \frac{(C_0 - C_t)v}{m} \qquad (2)$$

where q is the adsorbent removal capacity of the given contaminant; C_0 is the initial and C_t is the equilibrium concentration of the given contaminant (mg dm⁻³); v is the volume of solution (dm³) and m is the weight of the adsorbent (g) [50].

2.4. Analytical methods

Table 4 summarizes the analytical methods used during the experiment.

2.5. Statistical Analyses

Statistical analyzes were carried out using the IBM SPSS Statistics 26 package. The basic descriptive statistics were analyzed with the Kolmogorov–Smirnow test, the Pearson r correlation analysis, and the non-parametric Spearman rho correlation analysis. The level of significance in this chapter was considered to be $\alpha = 0.05$.

3. Results and discussion

3.1. Evaluation of the effects of using biochar filled filters to remove ammonia generated during composting

While analyzing the output parameters of the compost mix (Table 3), it can be seen that the moisture content – 57.91% – was within the optimal range (45%–65%) [51]. The pH of the obtained mixture was close to neutral and constituted a favorable environment for the development of microorganisms. According to the literature, a C/N ratio in the mix (within 25–35) favorable for the composting

Table 2
Physicochemical parameters of selected substrates of compost mixtures

Type of sample	DS, %	MM, % d.m.	OM, % s.m.	M, %	C/N	pH
Straw	90.99	1.87	98.13	9.01	109.36	6.12
Chicken manure	30.65	45.64	54.36	69.35	8.20	5.69
Kitchen waste	17.60	6.4	93.6	82.4	112.05	8.23

MM – mineral matter, M – moisture, OM – organic matter, DS – dry mass.

Table 3
Selected parameters of the compost mix introduced into the bioreactors (average values of the mix in stages I and II)

DS, %	42.09
MM, % d.m.	11.97
M, %	57.91
OM, % d.m.	88.03
C/N	25.90
pH	7.45

process was obtained. However, for the purpose of the study, a lower C/N ratio value that would increase the likelihood of ammonia emissions would be more desirable [43,44]. The compost C/N ratio determines the nitrogen leakage from the compost mass in the form of ammonia. When the C/N ratio is higher than 20:1, its emission decreases. A higher C/N ratio reduces the release of ammonia, and a lower C/N ratio speeds up its emission. The release of ammonia during composting begins when the process temperature rises above 45°C. Its highest concentration is recorded in the first 2 weeks of conducting the process [45,52,53].

After a period of 10 d, a decrease in the share of organic substances in the mixture was noted in both research cycles, which is characteristic of the proper course of the composting process. Moreover, the share of mineral content increased in both research cycles.

On the basis of the results obtained, it was observed that after 10 d of composting, the pH increased to 7.60 (stage I) and 7.75 (stage II). The increase in the pH value at the beginning of the composting process may be due to protein mineralization, which consequently leads to an increase in the generated ammonia [54].

The C/N ratio slightly decreased from 25.9 to 24.35 (stage I) and 24.27 (stage II). This phenomenon is associated with the fact that the carbon contained in organic matter, along with the course of composting, is converted into CO_2, which results in a decrease in the carbon to nitrogen ratio. Similar levels of C removal during composting have also been reported in many studies [54,55].

The moisture content increased in both cycles by an average of 30% and exceeded 80%. The consequence of this

Table 4
Applied analytical methods

Parameter	Analytical method
pH_{H_2O}	1:10 v/v
Total carbon	by Multi N/C, Analytkjena (Jena, Germany)
Kjeldahl nitrogen	PN-EN 14671:2007
Moisture content	by oven drying at 105°C
Organic matter	by incineration in a muffle furnace at 550°C for 5 h
Biochar specific surface area	by ASAP 2420 V2.09A
Biochar morphology	scanning electron microscopy (SEM)
CO_2, O_2, and H_2S concentration	biogas analyzer DP – 27 BIO by NANOSENS
$N–NH_4$ concentration	Sample subjected to distillation for 5 min. As a receiver, 25 cm³ 0.1 M or 0.01 M HCl and 4 drops of methyl red were used. After the distillation, the samples were titrated with a strong base 0.1 M or 0.01 M NaOH (depending on the acid concentration previously used) until the distillate color changes to light yellow. The ammonium nitrogen content was calculated according to the formula: $$N_{NH_4} = \frac{f \times (v_{HCl} - v_{NaOH}) \times v_{pB}}{v_{pr}} \left[\frac{mg}{dm^3} \right]$$ f is the conversion factor depending on the acid concentration HCl, for 0.1 M HCl, $f = 1.4$, for 0.01 M HCl, $f = 0.14$, v_{HCl} is the volume used HCl during distillation, cm³, v_{NaOH} is the volume used NaOH during titration, cm³, v_{pl} is the sample volume in the scrubber, v_{pr} is the volume of sample used for testing.

could be disturbing the uniform flow of oxygen through the composted mixture. As Jędrczak 2007 states, it is possible to effectively compost the straw-containing mixtures at a humidity of approximately 85%. Fig. 4 shows what changes occurred in the basic indicators during the 10 d composting process [51].

During the composting process, daily measurements of the temperature inside the bioreactor were carried out. In order to maintain the reliability of the measurement, readings were taken at the same time. Readings were made using three probes located at different heights inside the bioreactor. However, the readings from the central probe S2 located 20 cm from the double perforated plate were the most reliable. In both stages, an increase in temperature was observed already in the first days of the conducted processes. The maximum temperature was recorded after the second day of the process – 64°C (stage I) and 60.9°C (stage II). The rapid increase in temperature may result from the bacterial decomposition activity in compost [51,54]. It was found that the next days of the process resulted in a decrease in temperature and they stabilized after about 6 d (on average to 31.9°C). These changes are presented in Fig. 5.

The monitoring of the gases (CO_2, O_2, and H_2S) produced in the composting process in both stages showed that an intensive process of organic matter decomposition took place already in the first days of the processes, as evidenced by an increase in the CO_2 concentration (18% – stage I and 17% – stage II) and low O_2 concentrations (0.2% on average). After the fourth day, the intensity of degradation processes significantly decreased, the O_2 concentration increased rapidly (on average to 17.2%) and CO_2 decreased on average to 2%. During the process, H_2S was not observed, which indicates good aeration of the mix and avoidance of anaerobic zones. The analysis of CO_2 and O_2 emissions and temperature in the process showed a link between these processes. The recorded temperature increase related to, among others with the intensity of organic matter decomposition processes coincided with the increase in the CO_2 concentration and decrease in the O_2 concentration in the analyzed gas products.

Gaseous ammonia is removed very effectively in the adsorption process. Its sorption capacity on commercial activated carbons ranges from 0.6 to 4.7 mg g^{-1} [56,57]. The problem with the use of activated carbon is associated with the costs of its production and regeneration. That is why biochar seems to be an interesting alternative. It is assumed that the amount of energy needed to produce commercial activated carbon from various sorbents ranges from 44 to 170 MJ kg^{-1} while for the production of biochar from 1.1 to 16 MJ kg^{-1} [50]. The biochar used in the process of ammonia sorption can be applied as an addition to soils to improve their fertility, instead of expensive regeneration.

In order to assess the effectiveness of the biochar used to remove ammonia, the quality of the post-process gases generated in the B2 bioreactor (without the filter column) was compared with the post-process gases generated in the B1 bioreactor equipped with the filter column. In stage I, the filtration column was filled with BBCh and in stage II – BSS.

The highest concentration of ammonia – 38.75 mg d^{-1} in the B2 bioreactor was recorded on day 4 of the process. It was found that the use of the BBCh biochar allowed its reduction to the level of 0.75 mg d^{-1} and on the biochar BSS to 0.97 mg d^{-1}. The BBCh biochar ammonia reduction ranged
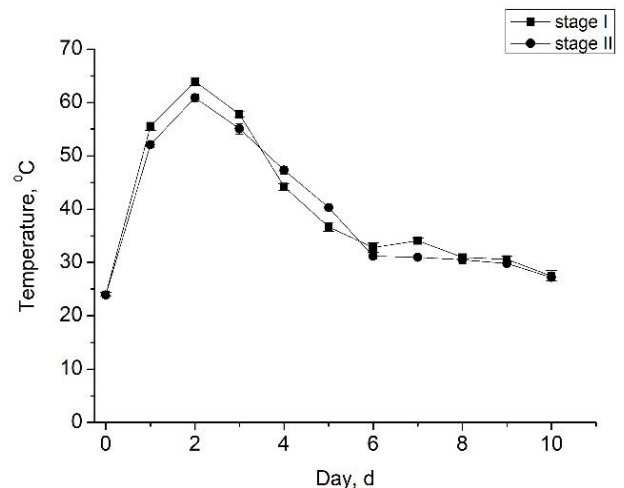
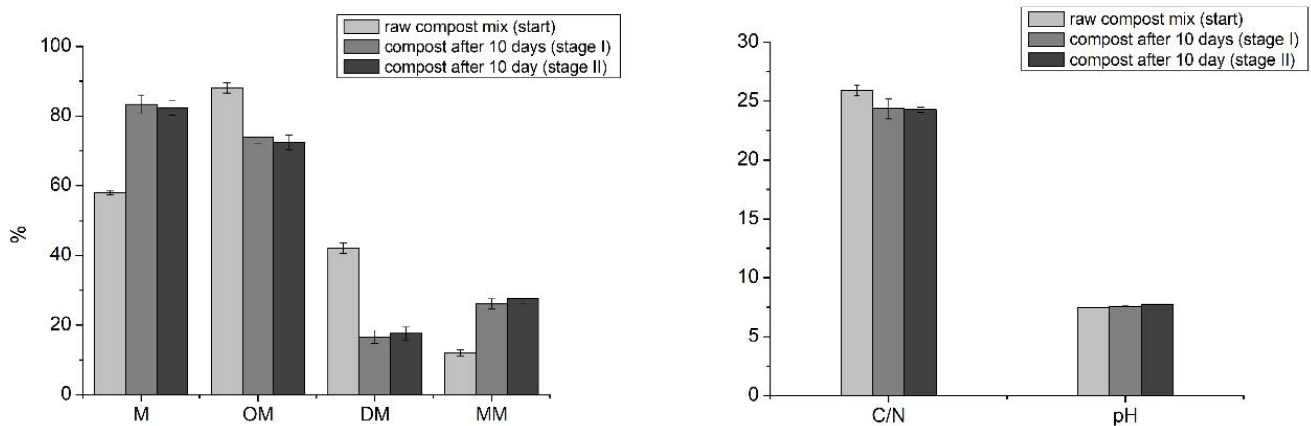Fig. 5. Change in temperature during the composting process.

Fig. 4. Changes of basic indicators during the composting process in stages I and II.

from 62% (day 2) to 98% (day 10). It was found that the reduction of ammonia on the biochar prepared from sewage sludge was on average 17% lower compared to BBCh. The degree of ammonia reduction ranged from 54% (day 2) to 74.9% (day 10). Additionally, the BBCh biochar adsorption process was more stable. This may be because the BBCh biochar was prepared at a higher temperature than the BSS biochar. According to reports, too low a temperature during pyrolysis may cause the filling of pores with tar and other amorphous decomposition products, which hinders the availability of pores and adsorption. The availability of pores increases along with the pyrolysis temperature [58]. The discussed changes are presented in Figs. 6a and b.

3.2. Removal of ammoniacal nitrogen from leachate on biochar

The leachate generated during composting had a pH of 7.9 and the concentration of ammonium was 315 mg dm^{-3}, on average. Wang et al. [59,60] observed an increase in NH$_4^+$ sorption on biochar when the pH of the solution is neutral. Therefore, in the first step, the pH of the leachate was corrected. It was also assumed that the basic compounds contained in biochar during agitation can be eluted and affect the pH of the purified leachate. The ability to absorb the ammonium nitrogen compounds by biochar is influenced by, among others competition between ammonium nitrogen and other substances for space on the biochar surface [32]. Fidel et al. [61] stated that such compounds can be precisely those leached from biochar. Moreover, the effluent from the composting process contains, in addition to the nitrogen compounds, several other substances that can potentially reduce the sorption effects of the nitrogen compounds [62].

The effectiveness of the ammonium nitrogen removal in the sorption process was started by determining the times of sorption equilibrium settling on the tested biochar. It was found that the sorption of ammonium nitrogen for both biochars was most intense in the first 2 h. The time to establish sorption equilibrium was faster on the biochar prepared from sewage sludge and settled after 1.5 h. In the case of the biochar from wood chips, the sorption equilibrium time was established only after 3 h. The discussed changes are presented in Figs. 7a and b.

When the smallest tested biochar dose (0.5 g dm^{-3}) was used, the degree of ammonium nitrogen removal for both biochar types was almost identical at 14% (BBCh I) and 17% (BSS). It was observed that a high degree of ammonium nitrogen removal for both biochar types was recorded for a dose of 2 g dm^{-3}. After 24 h of contact with biochar at this dose, the ammonium nitrogen value from 315 mg dm^{-3} decreased to 245.7 mg dm^{-3} (BSS) and 220.5 mg dm^{-3} (BBCh). Increasing the dose of biochar to 4 g dm^{-3} did not significantly affect the increase in ammonium nitrogen sorption. The ammonium nitrogen concentration decreased to 207.9 mg dm^{-3} – BBCh and 239.4 mg dm^{-3} – BSS. The degree of the ammonium nitrogen removal ranged from 17% (0.5 g dm^{-3}) to 34% (4 g dm^{-3}) for BBCh and from 14% (0.5 g dm^{-3}) to 24% (4 g dm^{-3}) for BSS. It was found that increasing the dose above 2 g dm^{-3} does not significantly increase the efficiency of the process (Fig. 8).

An increase in the dose of biochar does not have to result in an increased ability to remove N–NH$_4^+$ as reported by Bai et al. [35]. This may be because many of the surface regions that provided increased ammonium adsorption sites for adherence increased competition for ammonium. This may result in a reduction of the adsorption capacity in a unit biocarbon with an increase in its dose. It is found that the efficiency of ammoniacal nitrogen removal is higher from synthetic solutions than from real solutions. There are many other components in real solutions that compete with ammonium nitrogen for "sites" on biochar. In studies by Tang et al. [32], the ability to remove N–NH$_4^+$ from municipal wastewater was 1.2 mg g^{-1} of biochar (produced at 450°C), while with the use of a synthetic solution, this capacity increased to 1.4 mg g^{-1} of biochar. Liu et al. [19] found that the presence of other ions may interfere with the adsorption of ammonium nitrogen ions.

Increasing the doses of both biochar types was associated with a decrease in the sorption capacity. The highest sorption capacity was recorded at the dose of 0.5 g dm^{-3} which was 76.2 and 107 mg g^{-1} for BBC and BBCh, respectively.
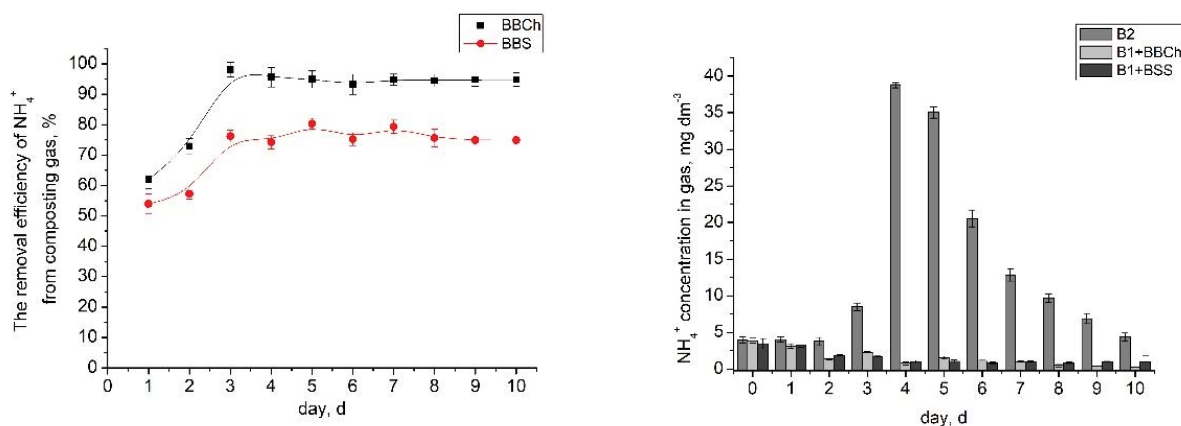

Fig. 6. Change in the degree of ammonia removal on biochar (a) and its concentration in post-process gas (b) during the composting process.
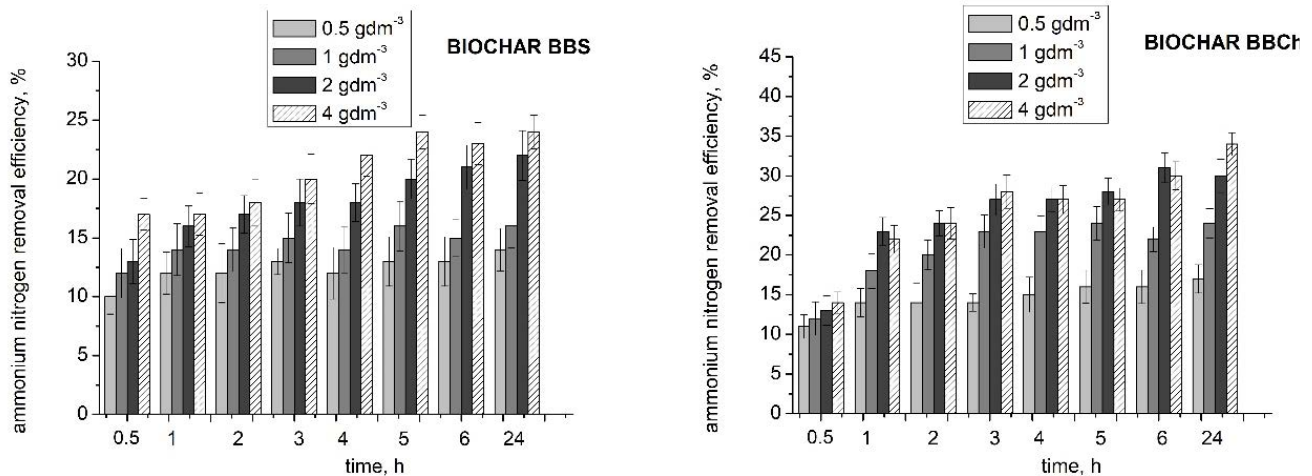
Fig. 7. Determination of biochar sorption equilibrium time BSS (a) and BBCh (b).

At the highest dose – 4 g dm⁻³, the sorption capacity decreased to 28.05 mg g⁻¹ (BBC) and 35.07 mg g⁻¹ (BBCh), respectively.

The Freundlich equation was used to describe sorption isotherms. Using the logarithmic form of this equation, the K_F and $1/n$ constants for the tested biochars were determined, and their values are presented in Table 5.

As can be seen in Table 5, the values of the correlation coefficient R^2 for the Freundlich equation are high, which may reflect a good fit of the model for the adsorption of ammonium nitrogen from the effluents. The isothermal constants $1/n$ and K_F are very important for determining the sorption capacity of pollutants from wastewater and for reducing the content of ammonium nitrogen on biochar. The $1/n$ slope depends on the sequence of changes in the ammonium nitrogen content reduction with the dose of biochar, while K_F depends on the degree of ammonium nitrogen removal by adsorbents [63].

It was found that the sorption process with 10% higher efficiency, on average, took place on the biochar prepared from chips (BBCh). This may result from a much higher specific surface of this biochar and higher temperature during the pyrolysis process.

Due to the low sorption effects achieved in the future, it is planned to intensify the process by modifying the used biochar (chemical or thermal). The sorption of nitrogen compounds from aqueous solutions is affected by the properties of biochar resulting from the type of substrate used and the temperature of the pyrolysis process used [28,34]. The biochar modification may have a positive effect on the N–NH₄⁺ sorption effects. As demonstrated by Jiang et al. [28] biochar characterized by a relatively low specific surface area (BET – 6.6 and 10.3 m² g⁻¹), modified with magnesium compounds showed good properties for the N–NH₄⁺ and P sorption. The adsorption of N and P was strongly correlated with the Mg content, while the total pore volume and specific surface area showed weak and moderate correlation.

In the first step of the statistical analysis, the distributions of quantitative variables were checked. For this purpose, basic descriptive statistics were calculated together with the Kolmogorov–Smirnow test examining normality.
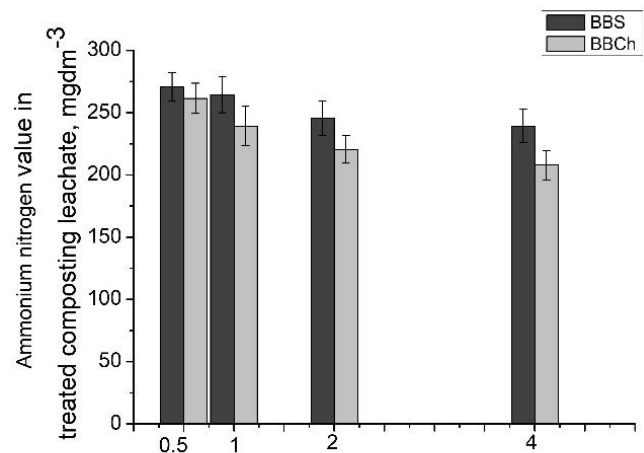

Fig. 8. Effect of biochar doses on the concentration of ammonium in purified leachate.

Table 5
Constants of Freundlich isotherms for ammonium nitrogen

Biochar	K_F, mg g⁻¹	$1/n$	R^2
BBC	4.40	5.026	95.16
BBCh	5.78	4.663	98.22

The result of the Kolmogorov–Smirnov test for all entered variables turned out to be statistically significant, which means that their distributions significantly differ from the normal distribution. However, it should be noted that the skewness of the distribution of the variables, the dose of biochar (g), and the degree of removal of N–NH₄⁺ removal does not exceed the conventional absolute value of 2, which means that their distributions are slightly asymmetric [64]. Therefore, if the other assumptions were met, parametric tests were performed. In the case of the absorption time variable, the skewness was higher than two, therefore the calculations with the participation of

Table 6
Basic descriptive statistics of the variables tested with the Kolmogorov–Smirnov test

	M	Me	SD	Sk.	Kurt.	Min.	Max.	D	p
Biochar dose (g)	1.88	1.50	1.34	0.66	−1.10	0.50	4.00	0.24	<0.001
Absorption time (h)	5.69	3.50	7.16	2.01	2.56	0.50	24.00	0.36	<0.001
Degree removal of N–NH$_4^+$ (%)	18.43	17.00	5.80	0.53	-0.64	9.00	34.00	0.12	<0.001

M – average; Me – median; SD – standard deviation; Sk. – skewness; Kurt. – kurtosis; Min. and Max. – the smallest and largest value of the distribution; D – statistics of the Kolmogorov–Smirnov test; p – significance.

Table 7
Correlation of the degree of N–NH$^+$ removal with the dose of biochar and the time of absorption

		Degree removal of N–NH$_4^+$ (%)
Biochar dose (g)	r Pearson	0.57
	Significance	<0.001
Absorption time (h)	rho Spearman	0.56
	Significance	<0.001

this variable were performed with a non-parametric test. The results of the analysis are presented in Table 6.

In the second step of the statistical analysis, the relationship between the% N–NH$_4^+$ removal and the dose of biochar and the absorption time was examined. The relationship between the biochar dose and the degree removal of N–NH$_4^+$ was investigated using Pearson's r correlation analysis. To investigate the relationship of the absorption time with the degree removal of N–NH$_4^+$, the non-parametric Spearman's rho correlation analysis was used. Pearson's r correlation analysis showed a statistically significant, positive, and strong relationship between biochar dose and degree removal of N–NH$_4^+$, as well as analysis with Spearman's rho test, revealed a statistically significant, positive, and strong relationship between absorption time and degree removal of N–NH$_4^+$. This means that a high degree removal of N–NH$_4^+$ from the solution coexists with higher doses of biochar and a longer absorption time. Details of the analyzes performed are presented in Table 7.

In the case of the effect of the biochar thermal modification on the improvement of its sorption capacity, the researchers' opinions are divided. In the study of Xu et al. [34] and Tang et al. [32] showed that the biochar produced at 700°C had worse NH$_4^+$ sorption than the biochar produced at lower temperatures. However, other studies report that during the production of biochar at low temperatures, pores may close or block, including ashes, and therefore it is advisable to run the process at higher temperatures [58].

4. Conclusions

The results of the conducted research showed that better sorption effects were obtained with the use of biochar produced from beech chips, which is probably due to their physicochemical properties. Increasing the sorption capacity of biochars requires a modification process

to obtain appropriate surface functional groups that determine the binding of substances removed. In the case of BSS biochars, it also seems necessary to activate them to obtain a larger specific surface area. The effectiveness of biochar in capturing pollutants depends on its specific surface. Its size, as well as the porosity of biochar or the number of functional groups, are influenced by its production temperature, heating rate, pressure, retention time, and ash content. The highest adsorption capacity in removing organic and inorganic compounds from wastewater is found in biochars produced at lower temperatures.

The obtained results confirm the potential of biochar as a sorbent for pollutants generated in the processing of biodegradable waste. They can be used in mechanical-biological waste treatment systems, increasing the efficiency of the composting process. They can be used as filling filters or biofilters purifying post-process gases before discharging them into the atmosphere. These sorbents can also be used to optimize the operation of wastewater treatment plants, for example, to remove ammoniacal nitrogen from leachate after dewatering sewage sludge. The use of biochar at this stage may prevent an excessive increase in nitrogen load in the sewage caused by the return of leachate to the beginning of the technological line of the treatment plant. Nitrogen-enriched biochars can be a potential soil improver. To investigate these possibilities, it is planned to conduct further studies on the sorption of ammonium nitrogen from the leachate (using modified and unmodified biochars) and the potential application of biochars used in the sorption process. The analysis of Pearson's r correlation showed a statistically significant, positive, and strong relationship between the doses of biochar used and the processing time with the degree of ammonium nitrogen removal. This confirms the necessity of research on the selection of doses, the type of biochar, and the duration of the process to remove various types of pollutants from wastewater.

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