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Preliminary studies on odor removal in the adsorption process on biochars produced form sewage sludge and beekeeping waste

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Abstract: The paper presents the preliminary study of n-butanol removal in the adsorption process. The main objective of the research was to assess whether and to what extent biochars produced from selected organic waste materials are suitable for odor removal. Biochars produced from dried sewage sludge and beekeeping waste were tested in the adsorption process. At first, raw materials were pyrolyzed and then modified with a 25% $ZnCl_2$ solution or a 30% H_2O_2 solution. The adsorption process was conducted using a model gas – the European reference odorant – n-butanol. The output parameter was odor concentration C_{od} [ou_E/m^3]. Odor concentration C_{od} values were obtained using a dynamic olfactometry method on T08 olfactometer. The solid byproducts of pyrolysis of digested sewage sludge and beekeeping waste may be used as adsorbents for the removal of n-butanol in the adsorption process. Adsorption performance of biochar from sewage sludge is better than biochar from beekeeping waste. Additional modification with H_2O_2 or $ZnCl_2$ increases the efficiency of the process, thus decreasing the required bed height for the elimination of odorant. The results of the studies confirm the findings of other authors that biochars derived from sewage sludge and other organic waste materials may be efficient sorbents in the removal of various substances from water or the air. Other biochars and methods of their activation should be tested. For practical reasons, the next stage of the research should be the determination of the adsorption front height and its migration rate.

Introduction

We continuously use smell, inhaling the fragrance particles that surround us. It is the only medium that reaches the higher structures through the olfactory bulb to the limbic system (hippocampus and amygdala) responsible for emotions and memories. The electrical impulses from the bulb evoke our sincere and strong feelings. Fragrances are perceived unconsciously, and one cannot understand them. We react positively or negatively to the scent, not knowing the source of it. Some smells are pleasant, and some are disgusting. A sense of smell is a social alarm system, quickly informing us about a potential threat. Odors during prolonged exposure result in discomfort, depression, insomnia, lack of appetite, headaches, respiratory problems, nausea, and vomiting. External and individual factors influence odor nuisance. Odors emitted to the environment as a result of human activity are treated in European legislation as pollution, in many countries subject to legal regulations (Sówka 2011). Pollutants with low detection thresholds and small concentrations often determine the odor impact of objects. Therefore, it is necessary to find and apply an efficient method to remove or decrease odor nuisance. One of them is the adsorption process on activated carbon.

Activated carbon (AC) may be produced from any material containing significant amounts of elemental carbon. Commonly used as raw material for AC production are coal, wood, peat, as well as waste materials, e.g., coconut shells. The adsorbent usually has a complicated porous structure and a complex chemical nature of the surface, due to, among others, heteroatoms associated with the carbon skeleton, and, in particular, oxygen forming structures capable of ions exchange. Activated carbons, due to their highly disordered crystal structure and large specific surface, may be easily modified with thermal and physicochemical methods or their combination (Piekarski 2009).

Thermal modification of sorbents, depending on temperature, results in (Lach and Ociepa 2003):

- an approximately decrease of 10% in the mass of sorbent and pore volume, and an increase in the specific surface area (300°C);
- a reduction of acidic oxygen complexes, which enhances the adsorption of phenol from very dilute solutions (600°C);
- a decrease of about 15% in the weight of the adsorbent, with the constant pore volume and average pore radius, the specific surface area increases (800°C);

- a higher the specific surface area and total pore volume (from 850°C to 900°C);
- desorption of chemically bound oxygen and the formation of alkaline surface groups (above 1100°C).

Modification by surface oxidation may be conducted in a controlled or uncontrolled manner. Due to the oxidation process, the content of oxygen connections on the surface of activated carbon can increase by up to 30%.

The activation of carbon adsorbents with steam causes an increase in specific surface area, pore-volume, and a change in diameter of pores. An activation with hydrogen or steam causes a significant decrease in cation exchange capacity and increases anion capacity. Such modification causes a falling-off in the number of carboxyl groups and hydrophilic properties.

Carbons activated by oxidation processes with nitric acid and hydrogen peroxide obtain an enriched surface with acid--type polar oxygen groups and changed structural properties. Oxidation with nitric acid reduces the volume of sorbent pores, without changing the specific surface area and the average pore radius. On the other hand, oxidation with hydrogen peroxide causes an increase in a specific surface area, with almost the same pore diameter and a slight decrease in the total pore volume (Piekarski 2009).

An activation with ozone at any temperature creates acid--type functional groups. Such carbons retain mainly alkalis from aqueous solutions, instead of acids. Therefore, carbon sorbents can be treated as weakly acidic or weakly alkaline ion exchangers with low ion exchange capacity.

Municipal sewage sludge is a waste material, a byproduct of wastewater treatment. (Puchlik et al 2015) The chemical composition of sewage sludge is very variable and depends on the type of treated wastewater and the treatment processes used. They are characterized by high water content, a significant share of organic substances, as well as high ability to decay with the depletion of oxygen. This creates favorable conditions for the development of bacteria reducing sulfur compounds. The simultaneous fermentation and reduction of sulfur compounds makes the formation of large amounts of odorous compounds (hydrogen sulfide, carbon disulfide, methyl and ethyl mercaptans, dimethyl sulfide, dimethyl disulfide, trimethylamine, indol, and skatol) already at this stage (Hwang et al. 1995, Hvitved-Jacobsen et al. 2002, Wiśniewska et al. 2020). Also, heavy metals in a dissolved form, co-precipitated with metal oxides, as well as adsorbed or associated with biological residues, may be found in sewage sludge (De la Guardia and Morales-Rubio 1996, Latosińska 2014). The primary harmful heavy metals include cadmium, lead, arsenic, and mercury. Due to the high content of nitrogen, magnesium, and phosphorus, digested sludge is mainly used in agriculture for fertilizing soil and plants, land reclamation, and compost production, as well as for growing plants for energy purposes (Latosińska 2014, Szostek et al. 2018). Sewage sludge may also be used for the intensification of biogas production or disposed of using thermal methods, combustion of sludge containing more than 90% of dry matter, for example (Włodarczyk et al. 2014, Milik et al. 2016).

Some reports present the possibility of the production of biochars using sewage sludge (Chen et al. 2002, Tang et al. 2019) or other organic waste materials (Norouzi et al. 2020, Rauf et al. 2020, Kim et al. 2013, Bogusz et al. 2015, Ahmad et al. 2012, Guo et al. 2020, Chen et al. 2014) and its successful application for removal of various substances both from water or the air (Graham et al. 2001, Wen et al. 2011, Zhang et al. 2005). Biochars produced from organic waste materials may also be used to improve soil properties (e.g. Titova & Baltrėnaitė 2020).

According to Polish Veterinary Inspection, there were approximately 1.63 million bee families in Poland in 2018. The modern beekeeping requires systematic reconstruction of beehives by introducing new frames with a honeycomb base. The share of replaced frames should be around 1/3. Withdrawn frames are melted. The products of that process are beeswax, which is a valuable product of many applications (e.g., re-production of honeycomb bases, wax castings, etc.), and bee slumgum, which is waste. The slumgum consists of wax (18–40%), and non-waxy parts, insoluble in water (brood cocoons, perga, propolis, remains of dead bees, etc.). Slumgum constitutes 10% of beeswax. One bee family produces approximately 2.8 kg of beeswax per year. So the total amount of slumgum waste produced in Poland is approx. 456 Mg/year (Curyło and Rybak 1972, Semkiw et al. 2018).

The paper presents the preliminary study of odor removal in the adsorption process. Experiments were conducted on biochars produced from sewage sludge and beekeeping waste.

Materials and methods

Sorbents produced from dried sewage sludge and beekeeping waste were tested in the adsorption process.

Sewage sludge comes from the municipal sewage treatment plant located in the West Pomeranian Voivodeship. Sludge treatment on that WWTP starts with a gravitational thickening. Then sludge is digested in an open separate fermentation chamber. The digested sludge is dewatered on centrifuges with the addition of electrolyte. Next, sludge is dewatered using a process of electroosmotic dehydrators, and then it is dried in the low-temperature belt dryer.

Beekeeping waste comes from a selected apiary producing and processing various types of honey. Apiary waste consists mainly of sieve wax and dead grubs collected from sieves.

Proximate properties of both materials are presented in table 1.

Table 1. Proximate analysis of waste materials used for production of biochars

Waste material	Moisture [%]	Volatile matter [%]	Ash [%]	Fixed carbon[a] [%]	VM/FC	Calorific value [MJ/kg]
Sewage sludge	7.6	39.8	36.7	15.9	2.5	13.0
Beekeeping Waste	17.1	69.4	1.7	11.8	5.9	24.0

[a] by difference

Sewage sludge and beekeeping waste were subjected to a pyrolysis process at the temperature of 650°C. The process parameters are similar to those presented in works of Lu et al. 2013, Lee et al. 2013 Angın 2013 and Shaaban et al. 2014.

The process was carried out in a two-chamber laboratory device (photo 1). The first chamber was used for heating the material. The second chamber was used for independent heating of obtained pyrolytic gas. Due to the construction of the pyrolysis device no inert gas was added during the process. The materials were heated for 1 hour to a temperature of 650°C in the pyrolysis chamber (at a temperature increase rate of about 10°C per minute). The temperature was kept for 3 hours. After cooling, the solid fraction remaining after the pyrolysis process was ground. Then part of produced biochars were activated/modified with a 25% $ZnCl_2$ solution and a 30% H_2O_2 solution, finally obtaining biochar form sewage sludge: not activated (BSSN), activated with $ZnCl_2$ (BSSZn), activated with H_2O_2 (BSSH) and biochar from beekeeping waste: not activated (BBWN), activated with $ZnCl_2$ (BBWZn), activated with H_2O_2 (BBWH). Samples of biochars were tested for ash content (PN-84/C-97555/08), moisture content (PN-84/C-97555/09), volatile matter content (PN-G-04516:1998) and iodine number (PN-83/C-97555/04). Next, photos of surface of biochars were taken using SEM.

The adsorption process was conducted using a model gas – the European reference odorant – n-butanol (concentration of 60 vppm). The gas was passed through the active carbon bed, maintaining a constant flow of vp = 0.5 dm^3/minute for t = 15 minutes. After that, a sample of gas for olfactometric tests was taken. The tests were conducted using variable heights of active carbon bed. So bed height H [mm] was an independent variable.

The output parameter was odor concentration C_{od} [ou_E/m^3]. Ou refers to the odor unit, and the E subscript means that the expressed concentration refers to the value determined following PN-EN 13725:2007 standard "Air quality. Determination of odor concentration by dynamic olfactometry" (PN-EN 13725:2007).

Odor concentration is defined as the concentration at which a person senses a single fragrant substance; it is called an individual olfactory sensibility threshold for that substance. The sensibility threshold has to be averaged for a population (sensibility threshold for a population). The odorant perceptibility threshold is such a concentration of odorant at which half of a population (or a representative group) can sense it. For individual substances, the odor concentration is the quotient of the odorant concentration by the threshold concentration value. In the case of mixtures of odors, the odor concentration can be defined as the fold of dilution of the test sample (with clean, odorless air) at which the olfactory sensing threshold is reached.

Photo 1. Two-chamber laboratory pyrolysis device

Odor concentration C_{od} values were obtained using a dynamic olfactometry method on T08 olfactometer, as described in (PN-EN 13725:2007, Sówka et al. 2013, Piecuch et al. 2015).

Results and discussion

Results of the analysis of tested biochars are presented in Table 2.

All biochars are characterized by low moisture content. Biochars produced form sewage sludge have high ash content and lower fixed carbon content. On the other hand, biochars from beekeeping waste are characterized by low ash content and much higher fixed carbon content. In both cases (beside BSSZn) VM/FC ratio is below 0.26, which indicates high resistance of biochars to thermal and biological decomposition (Lee et al. 2013).

SEM images of BSSN and BBWN presented in Figure 1 show that due to the diversity of the source material, diverse nature of the surface of materials resulted from pyrolysis.

Sewage sludge after the pyrolysis process (BSSN) is characterized by a heterogeneous structure that resembled various, rather big, irregular fragments with rounded edges, on which there are a few particles, most likely of mineral origin (Figure 1 A), which high ash content of 64.5% may confirm. Similar values of ash content were obtained by Chen et al. 2014 for the pyrolysis of sewage sludge, which confirms that almost all metal oxides and minerals remain in the biochar. The work of Chen et al. 2014 shows also that the specific surface area of biochars obtained in the pyrolysis process is much lower than in the case of active carbons. In our case, BSSN has iodine number 127 mg/g, while for the commercial active carbon (WD-extra) it is 923 mg/g. The modification of BSSN with $ZnCl_2$ and H_2O_2 caused an decrease of iodine number to 76 mg/g, which indicates even lower specific surface area. SEM images show that it is, most likely, caused by blocking of the adsorption surface with a big amount of mineral particles (Figures 2 A and 2 B).

On the other hand, the surface of BBWN is homogeneous, resembling tiles with sharp edges and even planes (Figure 1 B). Its specific surface area is lower than for BSSN and much lower than for WD-extra. The modification with $ZnCl_2$ and H_2O_2 did not change the value of iodine number. This proves lack of influence of this type of modification on the surface and structural parameters, which is also visible in the SEM images (Figure 2 C and 2 D).

Table 3 shows the results of olfactometric studies of odor removal in the adsorption process. The process was carried out on deposits of activated carbon produced by the

Table 2. Characteristics of tested biochars

Biochar	Moisture [%]	Volatile matter [%]	Ash [%]	Fixed carbon[a] [%]	VM/FC	Iodine number [mg/g]
BSSN	1.7	4.7	64.6	29.0	0.16	127
BSSH	2.3	7.2	64.2	26.3	0.27	76
BSSZn	3.4	9.7	64.8	22.1	0.43	76
BBWN	2.5	6.5	10.9	80.1	0.08	95
BBWH	2.7	6.2	11.5	79.6	0.08	95
BBWZn	3.1	6.6	12.5	77.8	0.08	95

[a] by difference

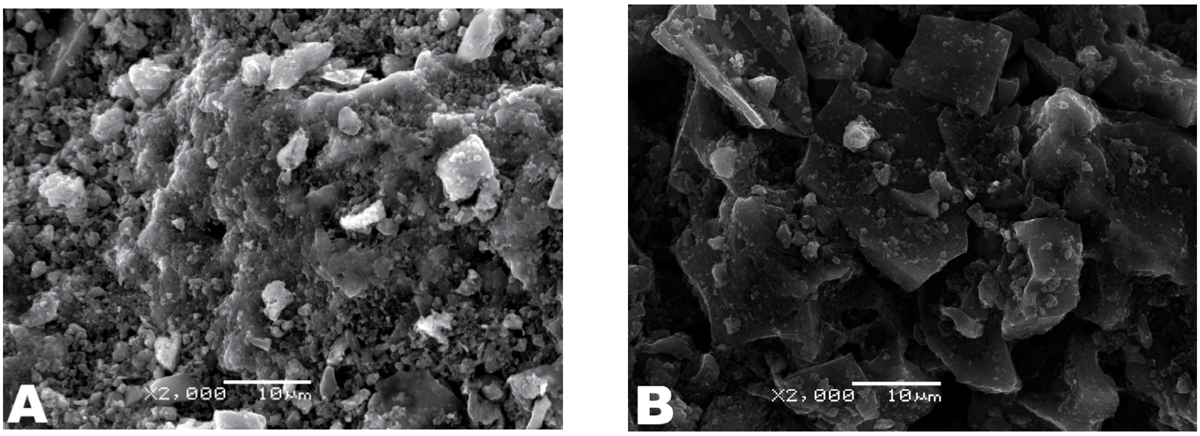

Fig. 1. SEM images of BSSN (A) and BBWN (B)

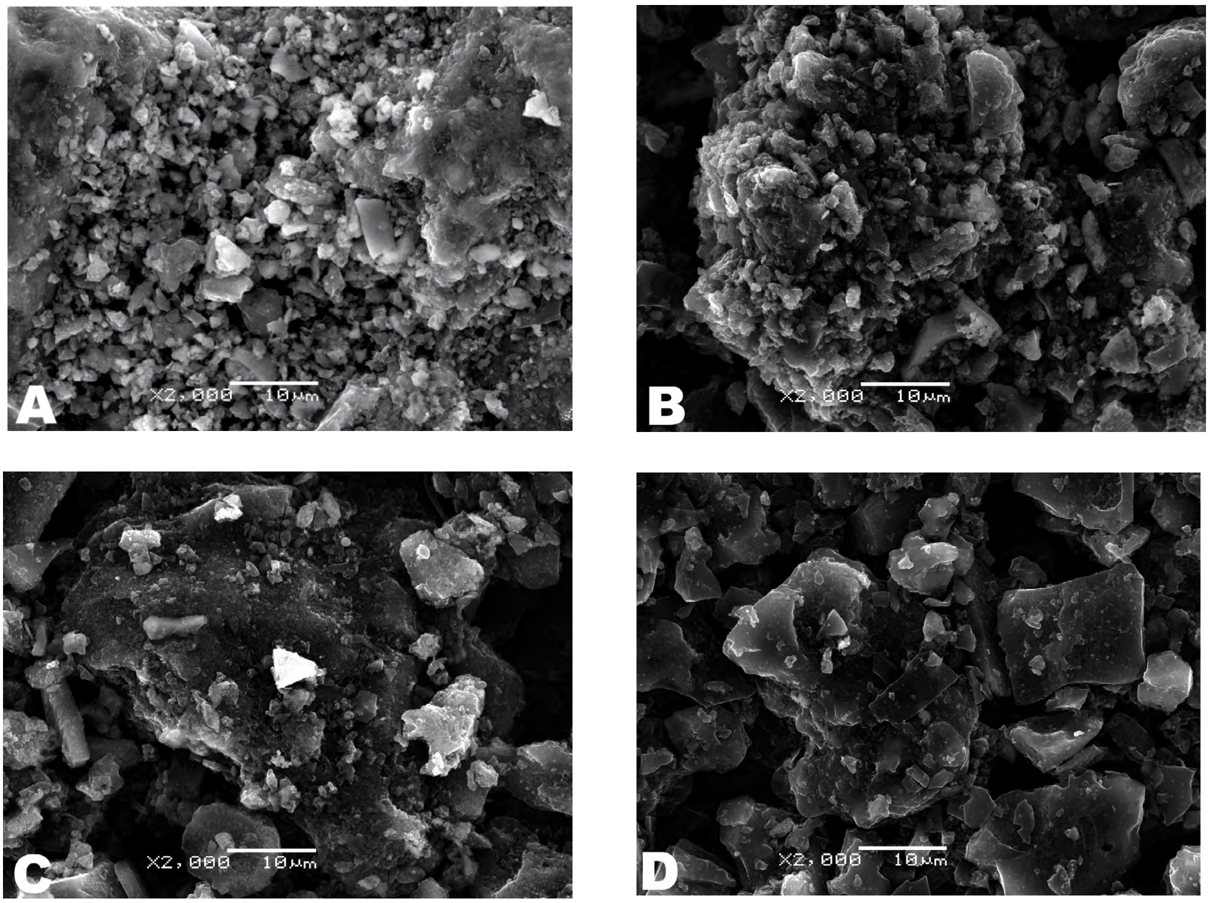

Fig. 2. SEM images of BSSZn (A), BSSH (B), BBWZn (C) and BBWH (D)

pyrolysis process from waste materials and activated in various conditions.

The charts presented in Figures 3 and 4 were developed based on data from Table 3. Preliminary data were subjected to non-linear estimation, according to Gauss-Newton in the Statistica program. The values of the coefficients of the selected functional equation of the form were obtained (Ignatowicz et al. 2016, Ignatowicz 2008):

$$C_{\%} = a_0H/(1+a_1H) \tag{1}$$

where:

$C_{\%}$ – percentage reduction of n-butanol odor perceptibility, [%],

H – height of the activated carbon bed, [mm],

a_0, a_1 – coefficients of the equation, [-].

Analysis of the results presented in Table 3 and on the graph – Figure 3, allows us to conclude that adsorption of n-butanol on biochars from sewage sludge, expressed as a percentage reduction in its perceptibility $C_{\%}$ [%], increases significantly along with bed height H [mm]. In the case of BSSN, a 100% reduction in odorant perceptibility was obtained on bed H = 60 mm high. That corresponds to a decrease in the odor concentration C_{od} from 330 ou_E/m^3 to 0 ou_E/m^3. An activation with H_2O_2 solution (BSSH) resulted in a small improvement in the adsorption process. A 100% reduction in odorant perceptibility was obtained on bed H = 50 mm high. The best results were acquired for BSSZn since a 100% decrease in odorant perceptibility was reached on a bed with a height of only H = 20 mm. The analysis of the properties of the tested materials allows to assume that n-butanol is retained in the adsorption process, with chemisorption as the more important phenomenon than the result of the expansion of the porous structure (Chen et al. 2014).

The values of the coefficients in equation (1) showing the percentage reduction in the perceptibility of n-butanol $C_{\%}$ [%] depending on the bed height H [mm] and the quality of the non-linear estimation of equations for carbon from sewage sludge activated under various conditions are presented in Table 4.

The graphs in Figure 3 and the quality of non-linear estimation (expressed by R^2 coefficient – Table 4) show that the equations sufficiently describe the measurement points obtained as a result of the tests. Similar values of coefficients a_0 and a_1 for BSSN and BSSH (Table 4) allow us to conclude

Table. 3. Odor concentration of n-butanol after adsorption process on various biochar beds

Biochar	Bed height H [mm]					
	0	10	20	30	50	60
	Odor concentration C_{od} [ou_E/m^3]					
BSSN	330	142	80	35	10	0
BSSH		128	72	29	0	–
BSSZn		57	1	–	–	–
BBWN		160	93	66	40	34
BBWH		128	65	23	0	–
BBWZn		85	38	0	–	–

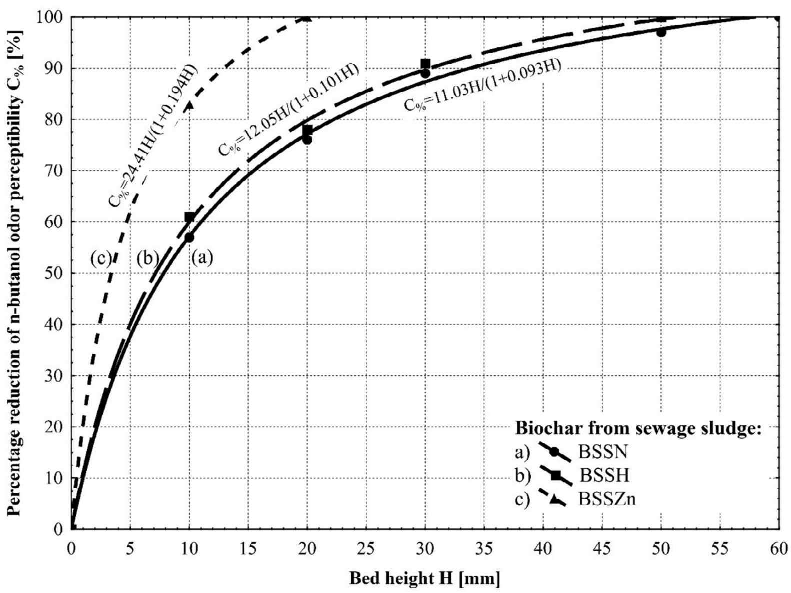

Fig. 3. Percentage reduction of n-butanol odor perceptibility $C_{\%}$ [%] after the adsorption process depending on the change in height H [mm] of BSSN, BSSH and BSSZn

that additional activation with H_2O_2 has brought only a slight increase of efficiency.

Analysis of the results presented in Table 3 and on the graph – Figure 4, allows us to conclude that the adsorption of n-butanol on biochar from beekeeping waste, expressed as a percentage reduction in its perceptibility $C_{\%}$ [%], also, in this case, increases significantly along with bed height H [mm]. A 100% reduction in odorant perceptibility was not obtained for BBWN in the tested range of bed height. Based on the estimated equation (Figure 4 a), a 100% reduction of odorant perceptibility may be obtained on a bed approximately H = 167 mm high. An activation with H_2O_2 solution (BBWH) resulted in an improvement in the adsorption process. A 100% reduction in odorant perceptibility was obtained on bed H = 50 mm high. And again, the best results were acquired for biochar activated with $ZnCl_2$ (BBWZn). Odorant perceptibility was 100% lower for bed H = 30 mm high. Despite different properties of biochars produced from sewage sludge and beekeeping waste the mechanism of n-butanol retaining seems the same. Also, in the case of biochars from beekeeping waste the phenomenon of chemisorption probably plays a significant role, apart from the adsorption process.

The values of the coefficients in equation (1) showing the percentage reduction in the perceptibility of n-butanol $C_{\%}$ [%] depending on the bed height H [mm] and the quality of the non-linear estimation of equations for biochars from beekeeping waste activated under various conditions are presented in Table 5.

Graphs in Figure 4 and the quality of non-linear estimation (expressed by R^2 coefficient – Table 5) also show that the equations sufficiently describe the measurement points obtained as a result of the tests. Similar values of coefficient a_1 may be observed for BBWN and BBWH. That indicates a similar course of adsorption in both cases but within a different range of values (different a_0 coefficients – Table 5). The values of a_0 and a_1 for BBWZn are significantly higher. That proves the higher effectiveness of that reagent also in the case of carbon from beekeeping waste.

Data presented in Figure 5 allows us to conclude that the pyrolysis process of tested waste materials allowed us to obtain biochars, which may be used for efficient adsorption of n-butanol from the air. Also, additional activation, especially with a $ZnCl_2$ solution, significantly increases their efficiency. The required bed height to eliminate n-butanol for BSSZN decreases by 66% and for BBWZn by 82%.

The results of the studies confirm the findings of other authors and other investigations (Chen et al. 2002, Tang et al. 2019, Graham et al. 2001, Wen et al. 2011, Zhang et al. 2005,

Table 4. List of coefficients values and the quality of the estimation of equations of reduction in the perceptibility of n-butanol $C_{\%}$ [%], depending on the bed height H [mm] (biochar from sewage sludge activated under various conditions)

Biochar from sewage sludge	Equation (1)		
	Coefficients		Quality of estimation
	a_0	a_1	R^2
BSSN	10.96	0.092	0.99
BSSH	12.05	0.101	0.99
BSSZn	24.41	0.194	1.00

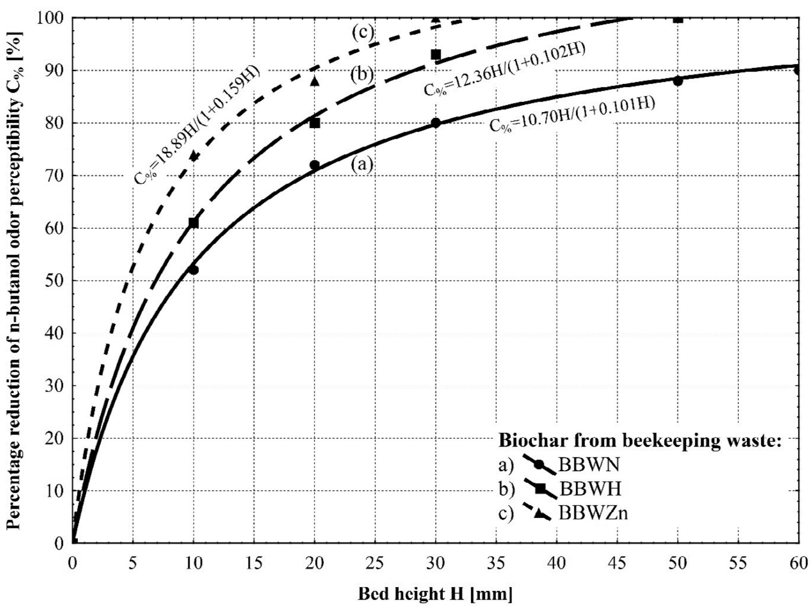

Fig. 4. Percentage reduction of n-butanol odor perceptibility $C_{\%}$ [%] after the adsorption process depending on the change in height H [mm] of BBWN, BBWH and BBWZn

Piekarski et al. 2021) that biochar derived from sewage sludge and other organic waste materials is an efficient sorbent in the removal of various organic substances from water or the air.

Conclusions

Results of the presented preliminary study allow us to draw the following conclusions:

1. Biochars obtained from pyrolysis of digested and dried sewage sludge and beekeeping waste may be used as adsorbents for the removal of n-butanol in the adsorption process. Adsorption performance of biochar from sewage sludge is better than biochar from beekeeping waste.
2. Additional activation using H_2O_2 or $ZnCl_2$ does not significantly influence the textural properties of biochars, although it decreases the required bed height for the elimination of odorant.
3. BSSZN has a 100% efficiency at bed height of H=20 mm. BBWZN has a 100% efficiency at bed height of H=30 mm.
4. Percentage reduction of n-butanol odor perceptibility C% vs bed height H [mm] is sufficiently described by the mathematical formula of Langmuir's isotherm, which is confirmed by coefficients of quality of estimation.
5. Other methods of activation of biochars should be applied in order to improve textural parameters. Also amount and types of functional groups on the surface of biochars as well as more detailed structural analysis of biochars should be performed.
6. For practical reasons, the next stage of the research should be the determination of the adsorption front height and its migration rate, which would allow for the application of tested adsorbents from waste materials in practice.

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Table 5. List of coefficients values and the quality of the estimation of equations of reduction in the perceptibility of n-butanol $C_{\%}$ [%], depending on the bed height H [mm] (biochar from beekeeping waste activated under various conditions)

Biochar from beekeeping waste	Equation (1)		
	Coefficients		Quality of estimation
	a_0	a_1	R^2
BBWN	10.70	0.101	0.99
BBWH	12.36	0.102	0.99
BBWZn	18.89	0.159	0.99

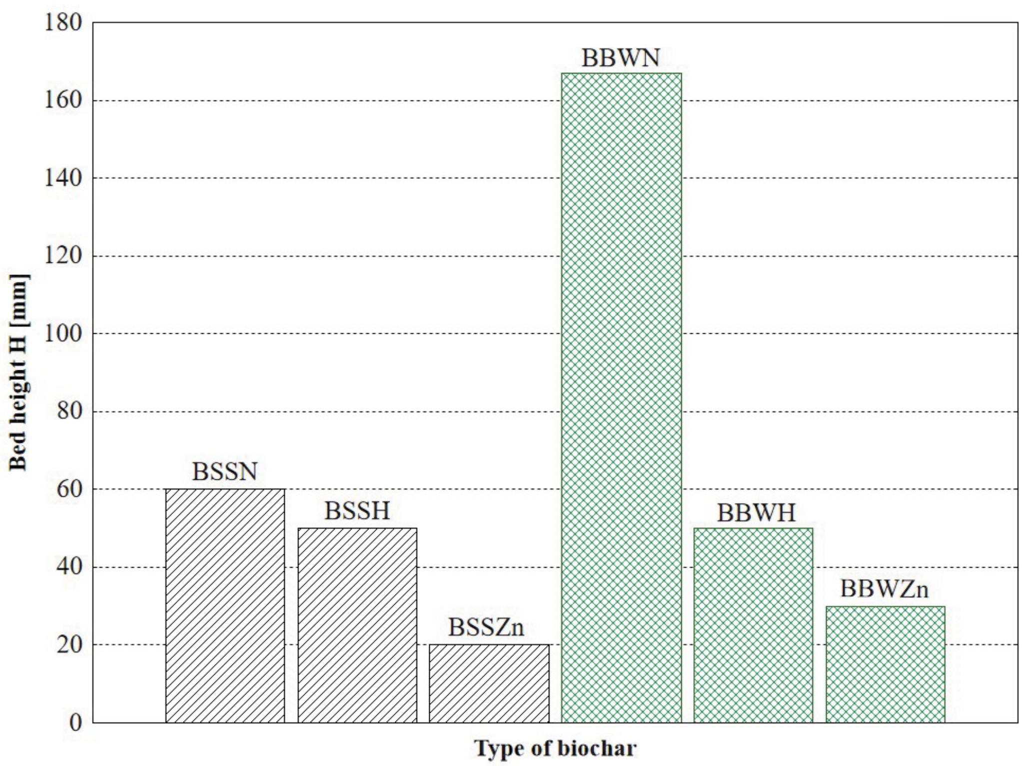

Fig. 5. Comparison of heights of the adsorption bed H [mm] which allow complete elimination of n-butanol perceptibility

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Wstępne badania usuwania odoranta w procesie adsorpcji na materiałach otrzymanych z osadów ściekowych i odpadów pszczelarskich

Streszczenie: W pracy przedstawiono wstępne badania usuwania n-butanolu w procesie adsorpcji. Głównym celem badań była ocena, czy i w jakim stopniu wybrane sorbenty wyprodukowane z wybranych odpadów organicznych nadają się do usuwania odorantów. W procesie adsorpcji przebadano sorbenty wytworzone z wysuszonych osadów ściekowych i odpadów pszczelarskich. Surowce początkowo poddano procesowi pirolizy, a następnie modyfikowano 25% roztworem $ZnCl_2$ lub 30% roztworem H_2O_2. Proces adsorpcji prowadzono przy użyciu gazu modelowego – europejskiego referencyjnego odoranta – n-butanolu. Parametrem wyjściowym było stężenie zapachowe Cod [ou_E/m^3]. Wartości stężenia zapachowego oznaczono metodą olfaktometrii dynamicznej na olfaktometrze T08. Stała frakcja po pirolizie przefermentowanych osadów ściekowych i odpadów pszczelarskich może służyć jako adsorbent do usuwania n-butanolu w procesie adsorpcji. Skuteczność adsorbentu z osadów ściekowych jest lepsza niż z odpadów pszczelarskich. Dodatkowa modyfikacja za pomocą H_2O_2 lub $ZnCl_2$ zwiększa wydajność sorbentów, zmniejszając tym samym wymaganą wysokość złoża do eliminacji substancji zapachowej. Wyniki badań potwierdzają wyniki otrzymane przez innych autorów, że sorbenty pochodzące z osadów ściekowych i innych odpadów organicznych mogą być skuteczne w usuwaniu różnych substancji z wody lub powietrza. W kolejnym etapie należy przetestować inne materiały i inne metody aktywacji. Natomiast dla warunków praktycznych należałoby obliczyć wysokość i szybkość migracji frontu adsorpcji złóż otrzymanych z materiałów odpadowych.