Biochar as a Sustainable Product for the Removal of Odor Emissions - Mini Literature Review

ŁUKASZ SOBOL*, ARKADIUSZ DYJAKON
Department of Applied Bioeconomy, Wroclaw University of Environmental and Life Sciences, Chelmońskiego St. 37a, 51-630 Wroclaw, Poland

Abstract: Odors are considered as one of the most important environmental problems that may adversely influence the quality of life of people affected by their interaction. Due to the multiple sources of emissions, combined with the abundance of chemical compounds classified odor nuisance, new methods of reducing odor emissions are sought while maintaining environmental neutrality. One potential option is to use biochar, a sustainable, carbonized solid product resulting from the thermo-chemical treatment of biomass and/or organic waste. Due to its valuable properties (in particular, high specific surface area, and microporous structure), this material can be used for sorption purposes. Although the issue of using biochar to remove odor emissions is relatively new, in recent years new research directions have been undertaken to determine the sorption efficiency of biochar not only as a direct adsorbent but also in alternative applications. Therefore, this paper aimed to review the most important directions of biochar management in the removal of odor-causing compounds and to highlight the current advances undertaken in this direction. It was distinguished that biochar can enhance odor mitigation by being an additive to compost, a biofiltration medium, a direct adsorbent, a soil additive, a substrate for the production of the odor-absorbing product, a dietary supplement, and a biocover. However, further research is needed to strengthen the range of greater use of biochar in practice.

Keywords: biochar, odor, adsorption, odor mitigation, environmental problems

1. Introduction
The sense of smell is considered as one of the oldest senses, which in the case of organisms with smell receptors, is characterized by a significant influence on the interaction with the environment in which they function [1]. The perceived olfactory sensations, depending on personal preferences, can arouse pleasant or unpleasant emotions and even lead to physical reactions caused by the involvement of the trigeminal nerve and higher levels of the brain [2].

Smells that bring a person into a state of subjective discomfort in the physical and mental sphere are referred to as odor nuisance (odors). Odorants are an extensive group of chemical compounds that can smell significantly different. In addition, the smell of odorant mixtures is highly diversified, which often makes it very difficult to predict a specific smell [3]. According to Rappert and Müller [4], odorants include both volatile inorganic compounds (VIC) and volatile organic compounds (VOC). Among the most popular odorants, there are nitrogen compounds and sulfur compounds, mainly dimethyl sulfide ((CH₃)₂S), dimethyl disulfide (CH₃SSCH₃), hydrogen sulfide (H₂S), organic sulfur compounds such as mercaptans, indoles, scatols, and organic acids. Other important groups are aldehydes and ketones [5,6]. Their emission is one of the most important environmental problems because it leads directly to [7,8]:

• health problems (nausea, irritability, headache, difficulty concentrating, lung diseases, eye infections, depression, breathing problems, vomiting, nausea),
• discomfort and lowering the safety of individual people who are exposed to odorants,
• social conflicts, inability to do business activity,
• inability to use real estate or properties that are directly exposed to odorants.

Such destructive effects of odorous gases, together with the growing interest of citizens in air quality and the multi-source nature of odor substances emissions, have made them one of the most common and serious environmental problems requiring reduction or complete elimination [9]. The issues related to
the formation and perception of odors should be classified as a significant threat to sustainable development, which should be characterized by care for sound and aromatic quality of life [10]. This problem can be considered not only in the ecological aspect but also in the social one [11]. The potential for odor nuisance in numerous industries means that investors undertake, at various stages of planning, implementation, and operation of a given installation, multi-directional techniques to reduce odor emissions, which include, among others: spatial planning, technical activities, odor masking, methods to reduce odor emissions.

A promising, cost-effective method of reducing odor emissions is the use of biochar [12] - a material with properties similar to charcoal, for the production of which substances of organic origin are used - e.g. wood, crop residues, food waste, grass, etc. Contrary to the previous solutions used in the elimination of odor-generating substances, the advantage of such action is the management of bio-waste, which is also important from the point of view of sustainable development as well as circular economy, and effective use of by-products. The use of biochar can stimulate the transition to the sustainable removal of undesirable chemical pollutants, synergistically solving the problem related to the management and disposal of biomass waste used for the production of biochar. Compared to the traditional adsorbent - activated carbon, it does not require an activation process, and therefore it limits the use of large amounts of chemicals (in the case of chemical activation) or the use of more energy related to the production at a higher temperature (in the case of physical activation). It is also worth adding that according to Kumar and Bhattacharya [13] the use of biochar can be particularly helpful in achieving the various goals set out for sustainable development, such as [14]: “Climat Action”, “Good Health and Well-Being”, “Life on Land”, “Sustainable Cities and Communities”.

Despite the fact that the use of biochar to mitigate odor emissions is relatively new, due to the efficiency and advantages of the process, many research directions have been undertaken, related to the possibility of implementing biochar into various odor reduction techniques. Therefore, to have a better picture of the state of the art in this subject, the aim of the paper is to review and discuss the most important methods related to the application of biochar as a balanced sorbent to reduce odor nuisance.

2. Materials and methods
The website Web of Science (database: Web of Science Core Collection) was used to carry out a literature review. The search period was set from 01/01/2000 to 01/03/2022. The review approach focused on the collection of systematic methods and the efficiency of using biochar to remove odor emissions. Keywords used in the literature search included "biochar" OR "biocoal" OR "biocarbon" AND "odor" OR "odour". Then, the articles meeting the imposed criteria were properly selected, distinguishing specific methods of using biochar. In the case of some articles, the snowball method was used, which allowed enriching the review with articles not found in the database.

3. Results and discussions
3.1. Sorption characteristic of biochar
Biochar is defined as carbon-rich material produced by pyrolysis and torrefaction - thermochemical processing of biomass, mainly without oxygen, in the temperature range of 200-700°C [15]. The resulting product is characterized by a high degree of energy densification, hydrophobicity, good susceptibility to grinding and compacting in the pelleting process, porous structure, extended specific surface, high content of organic carbon, active functional groups, as well as high cation exchange capacity [16-18]. The change in the physicochemical properties of the biomass is attributed to reaction mechanisms, which include dehydroxylation of hemicelluloses, deacetylation, decarboxylation of xylan-containing hemicellulose polymers, depolymerization, and demethoxylation from cellulose and lignin. On the other hand, the decrease in mass during thermal decomposition causes decarbonization, dehydrogenation, and deoxidation of biomass [19]. As a result, biochar is an attractive product that can be used, among others, as fuel in combustion and gasification systems, and as an additive to the soil, fodder, silage, and material enhancing the efficiency of composting and biogas production. Currently,
however, the very good sorption characteristics of biochar mean that it is usually produced as an economical and environmentally friendly sorbent to reduce odor emissions [20].

It is assumed that there are two main properties associated with increased sorption efficiency, namely: the large specific surface area and the microporous structure of biochar [21]. As a rule, the values of these parameters increase with increasing pyrolysis temperature [22,23]. During the process, depending on the type of substrate, the release of volatile substances at different rates and the formation of a larger number of pores that have been blocked so far [24]. The direct increase in the porosity of biochar is associated with the decomposition of lignin, the rapid release of H₂ and CH₄, as well as the aromatic condensation reactions that occur with increasing temperature [25,26]. As reported by Zhao et al. [26] some of the amorphous carbon structures are formed from cellulose degradation. In the case of the second parameter, the value of the specific surface area increases during pyrolysis due to the decomposition of cellulose, hemicellulose, and the formation of channel structures [27]. The content of non-flammable components (moisture, ash), which are highly differentiated depending on the input material, also has a significant impact on the specific surface. According to Ronsse et al. [28] increasing the number of inorganic substances causes a negative correlation with the specific surface area of biochar. It is also worth emphasizing that other parameters, such as ash content, pH, the content of functional groups, and cation exchange capacity are also important properties in relation to the sorption characteristics of biochar [29].

Thanks to the above-mentioned features, in addition to the standard use of biochar as a sorbent in water solutions and soil, it can also be used for the adsorption of pollutants in gaseous form [30]. In recent years, more attention has been paid to the adsorption of odorous gases - including hydrogen sulfide (H₂S) and volatile organic compounds (VOC). From a practical point of view, the use of biochar to reduce odor emissions is highly efficient because multi-component pollutants are simultaneously removed, thus meeting the technical and economic efficiency aspects. The coordination of the removal of components with different chemical characteristics may favor the development of biochar as a sorbent for gaseous pollutants [30].

3.2. Directions of using biochar in odor removal

Figure 1 shows the most common ways of using biochar to reduce odor emissions. Based on the literature review, the seven basic methods are distinguished, in which biochar is an additive to compost, biofiltration medium, biocover, dietary supplement, fertilizer or soil additive, substrate for the production of odor-absorbing product, direct adsorbent.
3.2.1. Compost additive

The first of the distinguished methods is the use of biochar as an additive to compost. The conducted research has shown that the addition of biochar in the right proportion is effective in reducing the emission of odorous substances. Steiner et al. [31], by mixing compost with biochar (20% w/w), achieved a reduction of NH$_3$ by 64% and a reduction of VSC by 71%. Duan et al. [32] when assessing the effectiveness of the addition of bamboo biochar on the degradation and humification of volatile fatty acids, showed that the addition of 10% biochar is able to stimulate the activity of microorganisms to catalyze the degradation of organic waste, reduce the amount of volatile fatty acids and odor emissions. Thanks to this it is possible to improve the quality of the product final. Awasthi et al. [33] confirmed that the addition of biochar at the level of 8-12% during composting biomass (straw) is able to reduce the effect of generating unpleasant odors, increase the degradation of volatile fatty acids and increase microbial abundance. The effectiveness of this method is also confirmed in practice [34].

A large part of the research is also devoted to reducing ammonia emissions after using biochar as a composting additive. During the co-composting of chicken manure and pine sawdust, Khan et al. [35] concluded that the use of biochar can reduce NH$_3$ emissions and nitrate leaching. Rong et al. [36] confirmed that the addition of wheat stalk biochar and rice husk biochar can statistically significantly reduce ammonia emissions by 53.4-88.7% and 62.5 and 89.3%, respectively. The details of various experiments related to this issue are presented by Akdeniz [37].

3.2.2. Biofiltration medium

Another method of using biochar is its use as a biofiltration medium. Baltrènas et al. [38] analyzed the possibility of using biochar from birch wood as a material for a biofilter bed along with the selection of four strains of organisms - incl. Aspergillus versicolor BF-4, Cladosporium herbarum 7KA, the yeast Exophiala sp. BF1, bacterium Bacillus subtilis B20. The performed tests showed that the xylene elimination capacity in the biochar-based biofilter is 103 g·m$^{-3}$·h$^{-1}$, and that of ammonia is 97 g·m$^{-3}$·h$^{-1}$, thanks to which the maximum efficiency of removing odors was 81-86%. The authors found that biochar can be successfully used in a biofiltration system to multiply the inoculated microorganisms and at the same time biodegrade acetone, xylene, and ammonia. An important aspect is also the fact that the authors emphasize that despite the biological effects of biofiltration are more important than the physical effects, the former is more important for compounds characterized by high values of Henry's coefficient, hence the selection of biochar with appropriate characteristics is a key element in the design of a biofilter. Baltrénaitė et al. [39] in their work present an analysis of the physicochemical properties of biochar based on the most important criteria for a biofiltration medium, integrating environmental properties, in accordance with the guidelines of the European Biochar Certificate. The authors suggest that lignocellulosic biochar may be more efficient for use as a biofiltration medium than other types of biochar. It is also worth emphasizing that it is possible to use biochar with biofiltration elements without using it as a carrier of microorganisms. Moreover, Li et al. [40], investigated the possibility of combining biochar and biospray filtration to remove unpleasant odors from compost, which is a mixture of straw and chicken manure, and revealed that the combination of biochar and spray biofiltration has significant potential for composting organic waste with high nitrogen content.

3.2.3. Biocover (surface application)

In this method, biochar is used both as a floating cover directly on a liquid or a layer applied to odor-causing solids (most often animal manures). In the first case, the research focuses mainly on the use of biochar to remove unpleasant odors from sanitary toilets and to store liquefied milk fertilizer. Senanu et al. [41] while studying the possibilities of using biocarbon covers to remove and suppress the smell of fresh fecal sludge, showed that thermally processed sawdust is able to reduce the reduction of H$_2$S and NH$_3$ by 96.2 and 74.7%, respectively. It was shown that biochar produced from local waste biomass can be a cost-effective and sustainable way to combat odor problems in dry sanitation. The usefulness of biocovers for the sorption of odors from liquids was also demonstrated by Dougherty et al. [42], who
investigated odor mitigation and gas emissions from liquid dairy fertilizer using biochar made from fir chips, a mixture of bark, and central wood. The last product reduced the mean headspace NH₃ concentration by 72-80%. In addition, the odor nuisance, as assessed by independent evaluators, was in most cases lower than compared of the control group. In the second case of using biocarbon covers, it is a layer applied to the surface of a solid, which most often consists of animal manures. It has been shown that powdered, surface-deposited porous corn straw biochar significantly reduces the amount of NH₃ emissions before the substrate is pumped out [43]. Generally, the surface application of a thin layer of biochar is able to reduce emissions of ammonia (NH₃), hydrogen sulfide (H₂S), greenhouse gases (GHG), and odorous volatile organic compounds (VOCs) such as phenol, indole, skatole, and p-cresol from stored swine manure [44]. These results have also been confirmed and validated on a pilot scale where similar types of compounds were assessed. Additionally, it has been observed that the cyclic application of biochar (every two weeks) shows a significant improvement in the mitigation of NH₃ and odorless VOC emissions, as opposed to increasing the dose with a single treatment [43]. Even more, it was shown that the use of biochar can potentially reduce the risk of inhalation exposure to H₂S, reducing peak concentrations of this compound below the general industrial peak limit. That makes an effective barrier to protecting farmers and animals from the toxic effects of these compounds [45,46]. However, not all cases of using biochar revealed a positive result. Ritz et al. [47] examining the effectiveness of the surface application of chars in limiting the volatilization of NH₃ from poultry litter, showed that the addition of peanut hull chars did not lower the NH₃ concentration in the air. Despite this, the authors obtained a positive result and a linear reduction in NH₃ concentrations after the use of acidified chars, which was probably the result of a combination of lowering the pH of the litter and immobilization of NH₃ by H₂SO₄ on the char [47]. After applying biochar to the litter, Flores et al. [48] also found no differences in ammonia emissions from litter. The storage time of the substrate and the dose of biochar applied also have an impact on reducing emissions [49]. Hence, it is assumed that the use of unactivated biochar may be a promising and cost-comparable option for the mitigation of odorous emissions from stored animal excrements. Another research team came to similar conclusions, investigating the possibility of reducing odorous VOCs (hexane, dimethyl trisulfide, phenol, p-cresol, and 2-methyl-3-pentanone) after applying a thin layer of biochar (10% w/w) on top of it. layers of cattle manure. The results showed a reduction in the concentrations used in samples containing biochar [50].

3.2.4. Diet supplement

Another alternative method of using biochar to reduce odor emissions is as a dietary supplement. Kalus et al. [51] assessed the impact of dietary supplementation with biochar in broiler chickens on the emission of ammonia and odorous compounds from manure. It is true that the conducted analysis showed that the feed additives significantly reduce ammonia emissions (up to 17%), but the reduction of other odor nuisance substances was statistically insignificant. It is worth noting, however, that in order to compare the aromatic concentration, an olfactometric test was performed with the highest doses of biochar additives to determine whether these treatments can mitigate the emission of odorous compounds to any degree (screening experiment).

3.2.5. Direct adsorbent

In recent years, more and more scientific works have been devoted to the use of biochar as a filter bed in the direct adsorption of odor-nuisance substances. These tests were performed with the use of many research methods and concern the reduction of various odorants.

Lee et al. [52] evaluated the adsorption of acetaldehyde and hydrogen sulfide (H₂S) in the Tedlar sack by biochar produced from empty fruit bunches. After placing 10 ppm of H₂S and aldehyde in a 10-liter bag of Tedlar with 0.1 g of biochar, the appropriate amount of time has waited and the concentration of odorants was measured using a gas detection tube (Gestec). It has been determined that biochar is a good adsorbent for these compounds, however, in order to increase its effectiveness, it must be subjected to chemical or physical activation.
Hwang et al. [53] assessed the potential of biochars made from poultry litter, swine manure, oak, and coconut shells at 350 and 500°C to remove 15 unpleasant odors of volatile organic compounds, consisting mainly of reduced sulfur compounds, volatile fatty acids, compounds phenolic and indole. The authors used a system of sorption columns on a laboratory scale. The conducted research showed that manure-based biochars were characterized by poor sorption capacity of dimethyl disulphide (DMDS) and dimethyl trisulphide (DMTS) - the two most common VOC emitted from swine manure, in contrast, to plant biomass-based biochar. Additionally, the authors pointed out that although biochar has less sorption capacity than activated carbon, it can provide additional income for users, as it can be sold as an additive to soil after use.

Sethupathi et al. [54] determined that biochar can be used to remove contaminants from biogas, such as carbon dioxide and hydrogen sulfide, with the desired lack of adequate methane adsorption. The authors analyzed biochars made of perilla, soybean stover, Korean oak, and Japanese oak at temperatures of 400 - 700°C. The experiment used four main fixed bed adsorber systems, a mass flow controller, a humidifier, and a biogas analyzer. Before that, Shang et al. [55] confirmed the ability to adsorb hydrogen sulphide by biochars made of camphor, rice hull, and bamboo at a temperature of 400°C using a laboratory H$_2$S removal stand. Recent reports also indicated that biochar obtained from rice hull, banana peel, and sawdust has high efficiency of H$_2$S removal, which may exceed 94% [56].

Piekarski et al. [57] performed preliminary studies of odorant removal in the adsorption process on biochar produced from dried sewage sludge and beekeeping waste. The process was carried out with the use of model gas - European reference odorant - n-butanol. Odor concentration tested by dynamic olfactometry method. The results of the research confirmed that biochar can be effective sorbents in removing various pollutants from the air or water. It is worth emphasizing, however, that the biochars were activated with 25% ZnCl$_2$ solution or 30% H$_2$O$_2$ solution. The authors suggest that it is necessary to test other types of biochar in the sorption of odor-causing pollutants and the methods of their activation.

Commercially available biochar is also tested for the removal of H$_2$S and VOCs. Initial pilot scale results confirm that most of the VOCs were below the detection limit (except for acetic acid) following the use of biochar in the swine gestation barn. The authors also determined that the adsorption capacity of H$_2$S by commercial biochar is high, and in addition, after the odor removal process, it can be recycled to improve the soil condition [58]. Kumar et al. [59] focused on the adsorption of 6 different VOCs (benzene, toluene, methyl chloride, xylene, chloroform, carbon tetrachloride) by unactivated biochars made of neem, sugarcane, and bamboo feedstock’s at temperatures of 350 - 550°C showed that process temperature variability and the type of raw material significantly influences the change of porosity and specific surface of biochar. Such a procedure is beneficial for the efficiency of VOC sorption.

3.2.6. Fertilizer/soil additive

Biochar can also be used as a fertilizer or soil additive, thus reducing odor emissions. The conducted research has shown that soils enriched with biochar are able to reduce the emissions of dimethyl disulfide (DMDS) - a soil fumigant for controlling pests with an unpleasant and easily perceptible sulfur odor [60]. The authors suggested that due to the modifications resulting from the application of biochar at a shallow depth of soil, the emission of DMDS to the atmosphere may significantly decrease. Nevertheless, this agent should be dosed with caution as it may also reduce the effectiveness of DMDS against soil pests. Other studies also confirm the effectiveness of biochar in reducing fumigant emissions such as 1,3-dichloropropene (1,3-D) and chloropicrin (CP) [61]. The authors, examining three biocarbon products (biochar made from almond shells at 550 and 900°C and coconut shells at 550°C), showed that all biocarbon treatments had a significant impact on reducing emissions by 38-100%. The reduction of fumigant emissions and the reduction of surface residue in soil were positively correlated with the adsorption capacity of biochar. It is also worth emphasizing that the application of biochar may increase the aroma of tobacco leaves [62].
3.2.7. Substrate for making the odor-adsorbing product

Biochar is also used as an additive in the production of odor-absorbing products. Vaughn et al. [63] created biodegradable cat litter by combining ERC fibers and juniper biochar. The addition of biochar reduced the emissions of 3-mercapto-3-methylbutan-1-ol (MMB), which is the main offensive volatile odorous compound present in the urine of cats. Sludge compost with the addition of biochar can also be used as an innovative casing material at waste sites [64]. Another alternative is the use of biochar as a perfume delivery system for air care in toilets [65].

4. Conclusions

Biochar is a sustainable product that can be successfully used in various odor-nuisance removal systems. The performed literature review showed that apart from the traditional use of biochar as a direct adsorbent filtering the gas stream, it can be used, among others, as a dietary supplement, compost additive, soil additive, biocover, biofiltration medium, and a substrate for the production of a product that absorbs the odor. In most cases, biochar was characterized as a cost-effective method of odor removal. The use of biochar to remove odor emissions could enhance its synergistic role as an adsorbent, while at the same time solving some of the problems related to the disposal and management of waste biomass. However, the efficiency and capacity of the processes influence many factors, such as the share and ratio of the biochar, its origin, and physical-chemical properties, as well as the operation condition of the process.

Unfortunately, not too much of the research has been carried out on a pilot scale so far, therefore it is still necessary to perform further tests to reach a competitive product in relation to traditional adsorbents used in practice.

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