Effect of bed height on efficiency of adsorption of odors from sewage sludge using modified biochars from organic waste materials as an adsorbent

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ABSTRACT

The paper presents the research on odor removal on biochars produced from municipal sewage sludge and beekeeping waste in the pyrolysis process and activated with ZnCl₂. Tests of odor neutralization were also carried out using the commercial activated carbon (AC) Organosorb 200-1 Wi, to compare its adsorption capacity with biochars from waste. The results of the studies confirm that modified biochar derived from sewage sludge and other organic waste is an efficient sorbent in the removal of odors. Biochars produced from beekeeping waste and sewage sludge in the process of pyrolysis and activation with ZnCl₂ are efficient, and may be compared with commercial AC Organosorb 200-1 Wi. The efficiency of the adsorption process E (%) depending on bed height H (mm) is sufficiently described by the mathematical formula of Langmuir's isotherm, which is confirmed by the coefficients of quality of estimation.

Keywords: Odor removal; Adsorption; Pyrolysis; Organic waste

1. Introduction

The olfactory ability is a genetically programmed alarm system that informs human beings about a potential threat. We perceive smells unconsciously, without knowing their source, we react positively or negatively. Odors may cause discomfort, depression, insomnia, loss of appetite, headache, respiratory problems, nausea, and vomiting. Odors emitted into the environment, as a result of human activity, are treated in European legislation as pollution and are subject to legal regulations in many countries [1]. On the other hand, the odor effect is often determined by pollutants of low concentration values and thus low odor detection thresholds; therefore, one of the best methods of purifying such pollutants is adsorption with the use of activated carbon (AC) [2]. Adsorption gives the best results on AC. ACs usually have a complicated porous structure and a complex chemical surface structure, which is obtained, among others, by heteroatoms bound to the carbon skeleton, in particular oxygen forming groups capable of exchanging ions. Due to the highly disordered crystal structure and large specific surface area, adsorbents are easily modified by thermal and physicochemical methods or their combinations. Such modification may result in a change in the sorbent mass, volume, and average pore radius, as well as a change in the specific surface area, and also acidic oxygen complexes [3,4]. Adsorbents can be produced from any material containing a lot of elemental carbon. The most common raw materials are coal, wood, and peat. ACs can also be produced from waste materials, e.g., coconut shells. An attractive solution may be the production of AC from waste materials such as municipal sewage sludge or beekeeping waste. Some reports present the possibility of the production of AC using sewage sludge [5,6] or other organic waste materials [7–13] and its successful application for removal of various substances from both water and the air [14–16].
Absorption processes with a chemical reaction, combustion, masking, and biological methods are also increasingly used [17]. The biofiltration process effectively removes odorous gases along with easily biodegradable organic compounds [18–20]. But biofiltration process is always accompanied by the phenomenon of adsorption, to a greater or lesser extent.

Most research concerning odor removal using adsorption is focused on volatile sulfur compounds, mainly hydrogen sulfide [21]. Martin et al. [22] reported that biochars from wood waste have favorable adsorption capacities for hydrogen sulfide relative to commercial ACs. Also, researchers reported that modified biochars produced from organic materials may be used for removal of hydrogen sulfide [23,24] or organic odorous compounds [25]. Real odors for example from sewage sludge are the mixture of many compounds. There are limited researches which deal with problem of their removal. Studies to explore adsorption of multi-compound odorants removal using adsorption are required to achieve cost effective and reliable techniques [21].

Municipal sewage sludge is a by-product of sewage treatment. Its chemical composition 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, and a high ability to decay along with the depletion of oxygen. That causes favorable conditions for the development of bacteria that reduce sulfur compounds. At this stage, the simultaneous fermentation and the reduction of sulfur compounds cause formation a large amount of odor-generating compounds, such as, hydrogen sulfide, carbon disulfide, methyl and ethyl mercaptans, dimethyl sulfide, dimethyl disulfide, trimethylamine, indoles, and scatols [26,27]. Due to the high content of nitrogen, magnesium, and phosphorus, the digested sludge is used mainly in agriculture for the fertilization of soils and plants, land reclamation and compost production, for the cultivation of rapeseed, and energy production [28,29]. Another new solution is the use of sewage sludge to intensify biogas production. The sludge can also be utilized thermally by incineration or by co-combustion, resulting in a high calorific value of the fuel. In the West Pomeranian Voivodeship, sewage sludge is used for energy purposes [30,31].

The modern apiary is based on the systematic reclamation and processing various types of honey. Apiary waste consists mainly of sieved wax and dead grubs collected from hives. Parameters of dried sewage sludge and beekeeping waste are given in Table 1.

Sewage sludge and beekeeping waste were subjected to a pyrolysis process at a temperature of 650°C. The process parameters are similar with ones presented in the works of Lu et al. [32], Lee et al. [33], Angın [34], and Shaaban et al. [35].

The materials were heated for 1 h to a temperature of 650°C in the pyrolysis chamber (at a temperature increase rate of about 10°C/min) with no inert gas added during the process. The temperature was maintained for 3 h. After cooling, the solid fraction remaining after the pyrolysis process was ground and modified. Process of modification was conducted using a 25% ZnCl₂ solution. The solution was slowly added to a 50 g samples of biochars from sewage sludge and beekeeping waste (stirring constantly) until a “spreadable” consistency of paste was obtained. Then, samples were dried for 24 h. Next, the biochar samples were rinsed with clean water (not removing the filtrate). The suspension was filtered, and then, biochar was heated in a furnace at 121°C for at least 30 min in order to remove leftover moisture. Obtained modified biochars were stored in an airtight container. For further test samples of biochar from sewage sludge modified with ZnCl₂ (SSB) and biochar from beekeeping waste modified with ZnCl₂ (BWB)

<table>
<thead>
<tr>
<th>Waste material</th>
<th>Sewage sludge</th>
<th>Beekeeping waste</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk density (g/dm³)</td>
<td>896</td>
<td>562</td>
</tr>
<tr>
<td>Moisture (%)</td>
<td>7.6</td>
<td>17.1</td>
</tr>
<tr>
<td>Volatile matter (%)</td>
<td>39.8</td>
<td>69.4</td>
</tr>
<tr>
<td>Ash (%)</td>
<td>36.7</td>
<td>1.7</td>
</tr>
<tr>
<td>Fixed carbon (%)</td>
<td>15.9</td>
<td>11.8</td>
</tr>
<tr>
<td>VM/FC</td>
<td>2.5</td>
<td>5.9</td>
</tr>
<tr>
<td>Calorific value (MJ/kg)</td>
<td>13.0</td>
<td>24.0</td>
</tr>
</tbody>
</table>

*By difference.*
as well as commercial Organosorb AC. Samples of SSB and BWB 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).

Comparative research on odor neutralization was carried out using the commercial AC DESOTEC Organosorb 200-1 Wi (Organosorb AC). It is a powdered adsorbent of a bulk density of about 280 g/dm³, produced from charcoal activated with steam.

Next, photos of surface of biochars and Organosorb AC were taken using scanning electron microscope (SEM).

Odor samples were taken from the heap of dried municipal sewage sludge and collected in the tank under the pressure of p = 3. The odor from the tank through a pressure line, a control valve, and a flow meter was directed to the adsorption process. The adsorbent was placed in a column with a diameter of d = 15 mm. The duration of the process was t = 15 min at a constant flow rate vp = 0.5 dm³/min. Then, gas samples for olfactometric tests were taken into polytetrafluoroethylene bags characterized by a lack of absorption and odor production. The concentration of odor in the bags was measured using dynamic olfactometry. One measurement of the odor concentration consisted of four series.

The independent variable was the bed height H (mm). At the same time, the resulting parameter was the odor concentration C od.

Odor concentration is defined as the concentration at which a person senses a single odoriferous substance, called the individual (for a given person) olfactory perceptibility threshold for this substance. The perceptibility threshold has to be an average value, a representative for the population (population perceptibility threshold). The olfactory perception threshold is such an odor concentration when half of the population (or a representative group) senses the odor when exposed to it. For individual substances, the odor concentration will be equal to the quotient of the odorant concentration and the threshold concentration value.

In the case of mixtures of odors, it is not possible to determine the odor concentration, similarly, it is not possible to decide on the olfactory threshold value. In this case, the odor concentration can be defined as the multiplicity of the dilution of the test sample (with clean, odorless air) needed to reach the olfactory perception threshold.

Odor concentration was measured using TO8 four stand dynamic olfactometer with the equipment. According to the standard, the tests were conducted in a quiet and isolated room with stable temperature and lighting conditions. The measurement team consisted of four evaluators and one operator. The evaluators were selected according to the guidelines using certified reference material (n-butanol in nitrogen). During the measurement, the evaluators signal when they smell the odor in the presented gas stream. The sample is diluted dynamically with odorless air. The initial dilution is odorless, and it is decreasing during the test. The presented dilutions were decreasing. Sometimes, a “blank” (clean, odorless air) is given to the evaluator instead of the tested sample. After two consecutive “I smell” signals from all four evaluators test is finished. The results are calculated for the measurement team Z – geometric mean of all individual measurements and C od.

Based on the odor concentration, the efficiency of the odorant adsorption process E (%) was calculated according to the formula:

\[
E = \left(1 - \frac{C_{od\text{e}}}{C_{od\text{i}}}\right) \times 100\% \tag{1}
\]

where \( C_{od\text{e}} \) is the odor concentration value after the adsorption process (ou/m³) and \( C_{od\text{i}} \) is the odor concentration value before the adsorption process (ou/m³).

The change in the efficiency of the adsorption process of odorant E (%) depending on the height of the bed H (mm) is described by the formula known in the mathematical notation as the Langmuir adsorption isotherm equation [37]:

\[
E = \frac{a_1 H}{(1 + a_2 H)} \% \tag{2}
\]

where E is the efficiency of the adsorption process of odorant (%), H is the height of the AC bed (mm), and \( a_1, a_2 \) are the equation coefficients.

3. Results and interpretation

Results of analysis of tested biochars and commercial Organosorb AC are presented in Table 2.

Biochars are characterized by low moisture content. SSB has a high ash content and lower fixed carbon content. On the other hand, BWB is characterized by low ash content and much higher fixed carbon content, its volatile matter to fixed carbon ratio ratio is below 0.26, which indicates high resistance of biochars to thermal and biological decomposition [33]. Also, parameters of BWB are more similar to commercial Organosorb AC, except for iodine number.

In order to characterize the morphology of the tested materials, SEM images of their surface are presented in Fig. 1.

SEM images of SSB and BWB presented in Fig. 1 show that various nature of the surface of materials obtained as a result of pyrolysis and modification is caused by the diversity of the source material.

SSB surface 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 (Figs. 1a and b), supported by higher ash content and bulk density. The ash content was 5 times higher, and the bulk density about 1.8 times higher than for Organosorb AC. Its surface was homogeneous in shape, resembling plates with sharp edges and even planes (Figs. 1e and f). Similar values of ash content in biochar from sewage sludge were obtained by Chen et al. [13], which confirms that almost all metal oxides and minerals remain in the biochar. As a result, a 3.5 times lower value of the fixed carbon was found in SSB than in Organosorb AC.

The work of Chen et al. also shows 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, SSB has iodine number of 76 mg/g, while for the commercial Organosorb AC it is 12 times higher.

SEM images of the BWB surface show that it is homogeneous, resembling tiles with round edges (Figs. 1c and d), on its surface there are sparse small particles of probably mineral origin. It is supported by ash content of 12.5%, 5 times lower than for SSB and about 2 times higher than for Organosorb AC. Fixed carbon content for

Fig. 1. SEM images of (a and b) SSB, (c and d) BWB, and (e and f) Organosorb AC, magnification ×500 and ×2,000.
both materials is similar. Also, specific BWB surface area is much lower than for Organosorb AC (iodine number for Organosorb AC is 9.5 times higher than for BWB).

Results presented in Table 2 and SEM images suggest that much lower iodine number of SSB and BBW than for Organosorb AC may be caused by blockage of surface area with mineral particles.

The results of olfactometric tests for the elimination of odors in the adsorption process are presented in Fig. 2. All the considered materials showed high adsorption capacity for the tested odorous gas; its average odor concentration was about 2,637 ouE/m³. The best adsorption capacity in the examined range of changes of independent variables was obtained for BWB (bulk density 562 g/dm³), then Organosorb AC (bulk density 500 g/dm³), and finally for SSB (bulk density 869 g/dm³). During the preliminary tests – adsorption on n-butanol – different results were obtained. Then, the best material was Organosorb, then SSB, and the worst was BWB. The preliminary tests also showed that the modification of biochars from waste materials with ZnCl₂ resulted in a significant increase in the adsorption capacity.

Based on the results and Eq. (1), the efficiency of the adsorption process of odorant \( E \) (%) was calculated. Coefficients of Eq. (2) were calculated using a non-linear estimation method, according to Gauss–Newton in the STATISTICA. The \( R^2 \) parameter allowed the evaluation of the quality of non-linear estimation. The results of the calculations are presented in Table 3, and the diagram shown in Fig. 3.

Values of \( R^2 \) coefficient given in Table 3 prove that the non-linear estimation method allowed for a good fit of the model to the data.

Table 3

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Eq. (2)</th>
<th>Coefficients</th>
<th>Estimation quality</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>( a_0 )</td>
<td>( a_1 )</td>
<td>( R^2 )</td>
</tr>
<tr>
<td>SSB</td>
<td>41.04</td>
<td>0.380</td>
<td>0.99</td>
</tr>
<tr>
<td>Organosorb AC</td>
<td>77.50</td>
<td>0.735</td>
<td>0.99</td>
</tr>
<tr>
<td>BWB</td>
<td>171.24</td>
<td>1.628</td>
<td>0.99</td>
</tr>
</tbody>
</table>

Fig. 2 presents calculated bed heights which allow complete removal of odor, during adsorption on tested carbons.

Based on the results of conducted tests, we may conclude that the selected modified waste materials may be used as adsorbents. They allow obtaining complete elimination of odors and are comparable with the commercial product Organosorb AC. In the case of BWB, a 100% reduction in odorant perceptibility was reached already at the bed height of 14 mm (decrease of \( C_{od} \) from 2,580 to 0 ouE/m³). Slightly worse results were obtained for Organosorb AC. Complete reduction of odorant perceptibility was achieved on a bed 28 mm high, i.e., two times higher than the bed of AC from beekeeping waste. At such bed height, the value of the \( C_{od} \) decreased from 2,435 to 0 ouE/m³. SSB turned out to be the least effective in the studied range of bed height changes – a 100% effectiveness of the adsorption process was not achieved. With a bed height of \( H = 42 \) mm (3 times as high as for AC from beekeeping waste), a reduction in odorant perceptibility from 2,896 to 2 ouE/m³ was obtained.

Fig. 2. Odor concentration \( C_{od} \) (ouE/m³) vs. bed height \( H \) (mm) for examined adsorbents.
Despite different properties of biochars produced from sewage sludge and beekeeping waste, the mechanism of odorants retaining seems to be the same for SSB and BWB. First of all sorption, probably supported by chemical reaction of sulfur volatile compounds with $\text{ZnCl}_2$ as well as the phenomenon of chemisorption.

The results of the studies confirm the findings of other authors [5,6,13–16,22–25,38] that biochars produced from sewage sludge or other organic waste materials, often modified, by a cost effective and efficient sorbent in the removal of various organic substances from water or the air. And often, they turn out to be better than commercial ACs.

Fig. 3. The efficiency of the adsorption process $E$ (%) depending on the change in the bed height $H$ (mm) of the analyzed adsorbents.

Fig. 4. Calculated adsorption bed height $H$ (mm) allowing complete removal of odor using tested adsorbents.
4. Conclusion

The results of the conducted experiments allow us to conclude:

- SSB and BWB produced from beekeeping waste and sewage sludge in the process of pyrolysis and activation with ZnCl₂ are efficient, and may be compared with commercial Organosorb AC.
- Adsorbent from beekeeping waste achieved 100% efficiency already at bed height of 14 mm. In comparison, adsorbent from sewage sludge requires a bed height of 43 mm high to reach 100% effectiveness.
- The efficiency of the adsorption process \( E \) (%) depending on bed height \( H \) (mm) is sufficiently described by the mathematical formula of Langmuir’s isotherm, which is confirmed by the coefficients of quality of estimation.
- 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.
- The next stage of the research should be the determination of the adsorption front height, its migration rate and ultimately the duration of the adsorption process until the so-called deposit breakthrough, which would allow the possible application of tested adsorbents from waste materials in practice.

Acknowledgment

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Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>SSB</td>
<td>Biochar from sewage sludge modified with ZnCl₂</td>
</tr>
<tr>
<td>BWB</td>
<td>Biochar from beekeeping waste modified with ZnCl₂</td>
</tr>
<tr>
<td>( C_{ode} )</td>
<td>Odor concentration value after the adsorption process, ou./m³</td>
</tr>
<tr>
<td>( C_{odb} )</td>
<td>Odor concentration value before the adsorption process, ou./m³</td>
</tr>
<tr>
<td>( E )</td>
<td>Efficiency of the adsorption process of odorant, %</td>
</tr>
<tr>
<td>( H )</td>
<td>Height of the AC bed, mm</td>
</tr>
<tr>
<td>( a_p ) ( a_t )</td>
<td>Equation coefficients</td>
</tr>
</tbody>
</table>

References

[23] F. Li, H. Wang, Y. Zhang, Q. Wang, Preparation of desulfurizing activated carbon from corn stalk and characterization of


