Assessing the Influence of Adsorbent Bed (Tree Bark) Parameters on the Reduction of Ammonia Emissions from Animal Husbandry

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Abstract

The influence of an adsorbent bed height made of tree bark on ammonia emission reduction was investigated under two scenarios: for constant mass of adsorbent and for adsorbent mass as a function of bed height. In both cases, measurements were performed on adsorptive beds of comparable height; other experimental conditions are presented in the part of the paper dealing with research methodology. The choice of tree bark as adsorbent material has been dictated by the results of preliminary research that was conducted on other biodegradable adsorbents in order to fulfill the basic assumption, i.e. that such materials, saturated with ammonia, should serve as natural organic fertilizer in plant production. The amount of ammonia absorbed on tree bark increased linearly with the increasing height of the adsorbent bed. These results were analyzed together with the data on reduced ammonia emissions, including the amount of adsorbed pollution and bed height. Moreover, the ratio of bed height to the adsorber inner diameter (h/dw) was used in data analysis. For the given optimal height of an adsorbent bed, the most appropriate time for replacing tree bark is when breakthrough first occurs.

Keywords: ammonia, animal husbandry, reduction of ammonia emission, tree bark
Material and Methods

Materials

Adsorbent: bark of a coniferous tree, i.e. common pine (*Pinus sylvestris* L.), was pre-treated by grinding in a grinder used for processing man-made materials. The size fraction retained on the 25x1.6 sieve of the laboratory grain sorter type SLA-00 was used for further analysis. The basic physical parameters of the bark, defined by means of methodology applied in soil science [11], were as follows: bulk density $\rho_d = 0.263\text{g/cm}^3$, specific density $\rho_s = 1.177\text{g/cm}^3$, porosity $n = 0.776$ and air-filled porosity $e = 3.472$. pH of tree bark in water is 3.95 [12].

Adsorbate: mix of $\text{NH}_3$ and air at concentration $C_o = 1.40 \pm 0.06\text{mg NH}_3/\text{dm}^3$

Aqueous ammonia solution was used as a source of $\text{NH}_3(g)$. This choice has been based on the literature data which indicate that from 51 [13] to 70% of ammonia excreted by animals can be found in their urine [14]. In aqueous solution, there is an equilibrium between free ammonia ($\text{NH}_3(aq)$) and ammonium ions ($\text{NH}_4^+$). The occurrence of free ammonia in solution can be described as below [13, 15]:

$$\text{NH}_4^+ \rightleftharpoons \text{NH}_3(aq) + \text{H}^+ \quad (1)$$

The amount of potentially free ammonia depends on the difference between ammonia concentrations in liquid $[\text{NH}_3(aq)]$ and gaseous phase $[\text{NH}_3(g)]$ above the solution’s surface.

$$\text{NH}_3(aq) \rightleftharpoons \text{NH}_3(g) \quad (2)$$

The value of dissociation constant $K_d$ depends on temperature; according to Jayaweera and Mikkelsen [16], $K_d$ for ammonia can be calculated from the following equation:

$$K_d = 10^{-0.0897 \cdot 2729/T} \quad (3)$$

where, $T$ is temperature [K].

The equilibrium between free ammonia in gaseous ($\text{NH}_3(g)$) and liquid phase ($\text{NH}_3(aq)$) is defined by Henry’s Law constant ($H_n$) [17]:

$$H_n = \frac{C_a}{C_g} \quad (4)$$

where, $C_a$ is concentration of the dissolved substance in liquid phase [mg/dm$^3$]; $C_g$ is concentration of the dissolved substance in the air [mg/dm$^3$].

Henry’s Law constant has been estimated based on the values found in literature. The selected Henry’s Law equations obtained by other authors are shown in Table 2.

Considering the comparability of values, simplicity of equations and a good fit of $[\text{NH}_3-N]$ concentrations usually found in animal feces (<1000mg/dm$^3$), the most suitable equations are those of Anderson et al. [18] and Sanders [20]. Anderson et al. published their equation in a scientific paper, while Sanders placed his on the Internet; it is the former equation that has been preferentially chosen by many for calculations. In the case of ammonia, the equation has the following form [13, 15, 22]:

$$H_n = \frac{2.395 \times 10^5 \cdot e^{(-4151/T)}}{T} \quad (5)$$

Table 1. Physicochemical properties of adsorbent*.

<table>
<thead>
<tr>
<th>Investigated property</th>
<th>Unit</th>
<th>Determined value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry mass content</td>
<td>%</td>
<td>91.69</td>
</tr>
<tr>
<td>Water content</td>
<td>%</td>
<td>8.31</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Content in dry mass</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>N, nitrogen</td>
<td>%</td>
<td>0.46</td>
</tr>
<tr>
<td>N-NH$_4$, ammonium nitrogen</td>
<td>%</td>
<td>0.03</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>%</td>
<td>&gt;0.01</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>%</td>
<td>0.17</td>
</tr>
<tr>
<td>CaO</td>
<td>%</td>
<td>2.31</td>
</tr>
<tr>
<td>MgO</td>
<td>%</td>
<td>0.06</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>%</td>
<td>0.01</td>
</tr>
</tbody>
</table>

* analysis performed by the Central Laboratory for Chemical Analyses, Institute of Soil Science and Plant Cultivation, State Research Institute, Pulawy

Table 2. The Henry’s Law constant according to various sources [15].

<table>
<thead>
<tr>
<th>Source</th>
<th>Equation*</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anderson et al. [18]</td>
<td>$0.865 \times e^{(4151/T)}$</td>
<td>mg/atm·dm$^3$</td>
</tr>
<tr>
<td>Jayaweera and Mikkelsen [16]</td>
<td>$183.8 \times e^{(-1229/T)}$</td>
<td>atm/mol</td>
</tr>
<tr>
<td>Olesen and Sommer [19]</td>
<td>$e^{(166.9 \times 621.0T/25.677lnT + 0.3597)}$</td>
<td>atm·dm$^3$/mol</td>
</tr>
<tr>
<td>Sanders [20]</td>
<td>$58 \times e^{(4101/7 + 1/298.15)}$</td>
<td>mol/atm·dm$^3$</td>
</tr>
<tr>
<td>Srinath and Loehr [21]</td>
<td>$3.564 \times 10^6 \times e^{(-0.0525T)}$</td>
<td>mg/atm·dm$^3$</td>
</tr>
</tbody>
</table>

* T is expressed in [K] in all equations
Considering the above premises, a solution was prepared by diluting 25\% ammonia (p.a. grade) with distilled water to the point when ammonia concentration in gaseous phase (i.e. in NH$_3$/air mix) at 293±1K reached 1.40±0.06mg/dm$^3$. In Fig. 1 the theoretical and experimental relationships between NH$_3(g)$ and temperature are presented. The gaseous ammonia concentration was determined by passing a known volume of the ammonia/air mix through a gas-washing bottle (Polezajew type, LABIT) filled with a given volume of 0.01n sulfuric acid (p.a. grade). The amount of unreacted sulfuric acid in the bottle was determined by alkalimetric titration [23].

Measuring Equipment

A laboratory set-up for measuring adsorption efficiency of the investigated ammonia adsorbate is shown schematically in Fig. 2. The set-up allowed the following analytical steps:

- Preparation of the ammonia/air mix containing the desired NH$_3$ concentration. Gaseous ammonia concentration above solution is a function of ammonia concentration in aqueous solution. Therefore, a 10dm$^3$ holding vessel filled with ammonia solution served as a source of adsorbate at very stable concentration during a series of studies.
- Application of various intensity flow of gaseous ammonia (i.e. ammonia/air mix of known volume; volume counted in 1dm$^3$ units) through the adsorbent layer. The application of choke diaphragm with experimentally selected discharge diameter (Fig. 2, element 6), and of the concurrently opened discharge valves (7 and 8) and 3-way valves (10 and 11) set in the direction of adsorber (3) determines the flow intensity of the ammonia/air mix at constant NH$_3(g)$ concentration via the rising level of aqueous ammonia solution in the dispenser of gaseous ammonia (2).
  After the solution reaches the 1.0dm$^3$ level in the dispenser (2), valves (7) and (8) are closed, and the 3-way valves are turned as follows: (10) in the direction of holding vessel (1)→by-pass without choke diaphragm; and (11) in the direction of holding vessel (1)→dispenser (2). The opening of discharge valve (7) and the solution level drop inside the holding vessel (1) allowing the resetting of the level of aqueous ammonia solution in the dispenser (2) to 0.0dm$^3$ and, consequently, returning to initial conditions. Dispensing of sequential portions of ammonia occurs periodically.
  - The steady flow of a known amount of NH$_3$ through different adsorbent beds characterized by specific parameters (e.g. porosity, height).

The ammonia/air mix, pushed by the rising level of aqueous solution in the dispenser (2), passes via a 3-way valve (11) and the connecting tube into a chamber located under the porous ceramic layer (Shot 101 sintered material; see Fig. 3) which results in a uniform permeation of the gaseous phase through the whole sintered area. Next, the stream of gas crosses the adsorbent bed located immediately on the porous septum of adsorber, and enters a gas-washing bottle...
Inside the bottle a complete reaction with the standard solution of $\text{H}_2\text{SO}_4$ takes place, which allows the quantitative determination of non-adsorbed ammonia. The dimensions of adsorbers with different diameters used in this study allowed for comparison of adsorption efficiency of beds with constant adsorbent mass and the variable bed height as a function of the adsorber’s cross-section area.

- The possibility of controlling ammonia concentration. The measuring set-up was designed in such a way as to secure the control of ammonia concentration in the ammonia/air mix before it enters the adsorber (scrubber 5 in Fig. 2) and after passage (scrubber 4).

Flow Intensity of Adsorbate

Adsorbate was dispensed periodically with a constant dynamic flow intensity ($1 \text{dm}^3/600\pm10\text{s}$), which is presented in Fig. 4, as a relationship between the amounts of dispensed ammonia/air mix ($V$) and time ($t$). A linear regression of the obtained experimental data was characterized by the high value of the coefficient of determination; the standard errors of the independent ($V$) and dependent ($t$) variables were 3.47 and 3.27%, respectively.

Research Procedure

Ten $\text{dm}^3$ of aqueous ammonia solution at a concentration of $2.15\text{g/dm}^3\text{N-NH}_3$ was prepared. A pre-weighted amount of ground and sieved adsorbate (coniferous tree bark) was placed in the adsorber. Next, the ammonia/air mix at the ammonia concentration of $1.40\text{mg/dm}^3$ (at $293\pm1\text{K}$) was passed periodically from the adsorbate’s dispenser through the adsorbent bed by means of gravity force, with the flow intensity $\theta=1\text{dm}^3/600\text{s}$. The ammonia/air mix ($C_o$) with altered chemical composition due to adsorption of $\text{NH}_3$ on tree bark ($C-C$) was then directed into a wet scrubber containing $0.01\text{n H}_2\text{SO}_4$, where the non-adsorbed ammonia ($C$) underwent complete chemisorption. According to the criterion found in literature, the adsorbate breakthrough point is reached when the adsorbate concentration after passage through the adsorbent bed is 5% of its initial concentration [24-26]. Therefore, a breakthrough ammonia concentration, measured in the ammonia/air mix discharged from the adsorber ($C$), has to conform to condition $C<0.05C_o$. The mean time of one break between sequential adsorption steps was $70\pm5\text{s}$; breaks mainly resulted from the level drop of aqueous ammonia solution in the dispenser to $0.0\text{dm}^3$ (see Fig. 2, element 2), and from the phase equilibrium stage (according to Equation 2).

Results and Discussion

The investigations of the relationship between the adsorbent bed height and adsorption were conducted under two scenarios, i.e. for constant mass of adsorbent ($m=\text{const}$; achieved by using adsorbers of different diameters – see Fig. 3) and for the adsorbent mass as a function of bed height ($m=f(h)$; achieved by using an adsorb of 22mm diameter). In both cases, the adsorbent bed heights were comparable and ranged from 10 to 110mm. The other parameters of adsorbate and adsorbent were identical, as described in Research methodology.

Considering the complexity of mathematical formulas that describe adsorption (e.g. variable adsorbate concentration in gaseous phase as well as in the form adsorbed onto a solid phase as a function of time $t$ and bed height $h$), the equation by Szilow and Lepin [27] was used to analyze the obtained data.
Assessing the Influence...

The $t_p$ values were determined for each sample from the linear regression equations of linear segments of exit curves; the computing method has been shown graphically in Fig. 5 for the function $C/C_0 = f(t)$. Estimation of the remaining parameters in equation (6) was only possible in the case of an adsorber of constant cross-section area, i.e. when $m = \rho_d V_k$ ($\rho_d$ is bulk density of bark [g/cm$^3$], and $V_k$ is bark bed volume [cm$^3$]). The function $t_p = f(h)$ for the experiments conducted under the “$h = \text{const}$” scenario does not reflect equation (6) (Fig. 6). The obtained linear increase of breakthrough time, and consequently the increased amount of ammonia adsorbed onto the tree bark, with the increasing sorbent bed height was analyzed in the context of ammonia emission reduction, including the mass of adsorbed pollution and bed height (Fig. 7). In Fig. 7a single trend lines form a bundle of parallel lines; the line for the bed height of 110mm is an exception as its slope is visibly smaller. It can be concluded that, for the comparable values of emission reduction of the investigated pollutant, proportionally larger gains of adsorbed ammonia had been achieved when bark beds of lower height were used in the adsorber.

Another relationship between the parameters of the analyzed adsorption system can be deduced from Fig. 7b. For constant mass of bark, the trend line for the largest bed height value is the steepest. This conclusion is based on two findings: 1) the mass of adsorbed ammonia characteristic for bed saturation is identical (within the limits of measuring error), i.e. about 50mg; and 2) the adsorbed ammonia mass, determined at breakthrough point, increases with the increasing adsorbent bed height.

$$t_p = kh - t_o'$$

where,

$t_p$ – breakthrough time, $h$ – adsorbent bed height, $k$ – kinetic coefficient, $t_o'$ – a parameter which depends on the exchange zone height and the time of adsorption front formation.

Fig. 5. Estimation of breakthrough time $t_p$ for the “ammonia/tree bark” adsorption system (bark bed height $h=80$mm)

Fig. 6. A relationship between breakthrough time ($t_p$) and bark bed height ($h$) for ammonia concentration 1.40mg/dm$^3$ in the NH$_3$/air mix and flow intensity $\vartheta = 1$dm$^3/600$s

Fig. 7. Reduction of ammonia emission as a function of the mass of gas adsorbed onto bark beds of different height $h=10-115$mm: a) $m = f(h)$, b) $m = \text{const}$
The pH value of the bark after adsorption process was 7.1. This means in practice that ammonia NH₃ undergoes change fully into NH₄⁺ form.

In the data analysis the ratio of the adsorbed bed height to the adsorber’s inner diameter (h/dₐ) was included; the ratio was different for each scenario. The highest ratio (about 7) was obtained for the largest value of bed height under the “constant adsorbent mass” scenario. Kostner et al. [28] achieved the highest reduction of ammonia for the h/d ratio of about 6 in the study in which a biofilter was used. Those authors formulated the thesis that for h/d>6 besides adsorption in the vertical direction (along the bed height) there are “dispersed” physico-chemical processes (in the directions perpendicular to the main stream of gas) which have a significant influence on the final reduction of pollution emission. The above thesis would explain, to a large degree, a disproportionately bigger reduction of ammonia emission obtained for the bark bed height of 110mm (see Fig. 7a). Moreover, disproportionately low values of ammonia reduction observed for lower values of bed height are also influenced by too short a time in which the breakthrough zone moves across the adsorbed bed of low h/d ratio. The shorter the time in which the breakthrough zone moves, the lower the probability that the entire adsorption area of tree bark will be efficiently used, particularly in the locations most peripheral to the main flow of contaminated air [29].

Example of Calculation for Livestock House

Assumptions:

- pig house with 10,000 fattening pigs,
- ammonia emissions from fattening pig houses: 108mg/h per animal [14], it is 9000kgNH₃/year per 10,000 fattening pigs,
- adsorption efficiency of the bark: about 0.01kgNH₃/kg bark (based on experimental results),
- cost of the bark: about 50PLN/1000kg (no transport from sawmill and grinding),
- bark density: ~300kg/m³,
- change of air in fattening pig house: on average 45m³/fattening pig h [30],
- maximal air flow velocity: 0.2m/s [30],
- maximal acceptable the pressure drop in ventilation system: 50Pa, it allows to apply the biofilter bed with depth of 1.5m [28].

Necessary bark quantity to adsorb 9,000kg of NH₃ per year realizing in experiments effectiveness of ammonia adsorption by bark, equal to 9·10⁶kg (3,000m³). This is close to 0.2% of the amount per year which is obtained as wood waste of coniferous trees in Poland [31]. For adsorption process the minimal bed depth of 2m is acceptable, allowing a quantity of pressure degree (pressure drop 100Pa/8m of air), even more, according to Kastnera et al. [28], wetted bed of biofilters makes higher flow resistance. Hence adsorber surface is 1,500m², and it gives the mean velocity of air flow per year (3.9·10⁹m²) equal to 0.08m/s.

Presented in above example the estimated calculations on ammonia adsorption by bark of coniferous trees allows us to define more data:

- the yearly bark cost for one fattening pig equals 4.5PLN, that is close to 1% of the price of 1 fattening pig,
- the cost of 1kg NH₃ adsorption equals 5PLN (1.3EUR) and in relation to the estimated costs for investmented biofilter equals to 20÷40EUR/kg NH₃ and exploited costs – 3.3EUR/kg NH₃ [32, 33] is competing against them, even if the transport cost of bark, its breaking and performing of simple installation (in compare to biofilters) are allowed,
- the profit in market farm of the natural nitrogenous fertilizer, in the amount of 7400kg as a pure nitrogen, that is optimal dose for area of 60÷70ha and minimum recovery of 1/3 cost for the bark purchase.

Conclusions

Empirical formulas are used in adsorber design quite often because they allow us to determine the adsorber dimensions as a function of adsorbent parameters. In this paper, the equation by Szilow was used to this end; basic coefficients for the equation were estimated under the initial conditions described in Research methodology. The presented results allow formulation of preliminary assumptions with regard to design of the air-purifying installation for animal husbandry buildings which constitute the main source of ammonia emission to the air. Based on the presented laboratory study, coniferous tree bark can be successfully applied to reduce ammonia pollution in the air. The bark is characterized by high efficiency of ammonia adsorption measured as the adsorbed gaseous phase per unit mass of adsorbent at the breakthrough point – 0.6mol NH₃/1kg bark. Comparison of this value with normal adsorption concentration on standard adsorbent, e.g. active carbon Darco – 4.2mol/kg [34], looks unfavorable only under quantitative aspect. Application of the bark, besides the obvious price preference and approachability, allows its further agricultural utilization and eliminates the necessity of extension of purifying installation, needed for regeneration of the bed (active carbon, zeolits) and further consequences of this. When the parameters of adsorbate (concentration and flow intensity) and adsorbent (constant particle size) remain constant, the reduction of NH₃ emission becomes a function of the adsorbent bed height. For a known mass of bark, the adsorption column height should be chosen in such a way that the ratio of bed height to the column inner diameter (h/dₐ) is about 6. However, when choosing such extreme values of the h/d ratio one should consider the effect of bark particle size on flow resistance in the air being purified on the adsorbent bed. The value of ratio h/d of the adsorber in the example differs from the optimal research value. That is the cause to prefer this
method of ammonia reduction in farms in places without any restriction contact time of the gas phase in adsorber or maximum drop pressure. For optimal adsorbent bed height, the most appropriate time for replacing tree bark is when breakthrough first occurs. It is so because further reduction of ammonia emissions takes place in the significantly less active adsorption centers on the bark’s surface, which results in quicker ammonia desorption during the next stage, i.e. bark preparation (e.g. via composting) for further processing into a natural organic fertilizer used in plant production. Besides low cost and good availability of bark, its use as described above gives basis to employ tree bark as ecological adsorbent. This method can well assist other solutions for the problem, particularly during storage of liquid animal excrements, finally minimizing the ammonia emission from areas with animal production.

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