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DECOMPOSITION OF HYDROGEN SULFIDE IN ORGANIC MATERIALS

Organic materials (mainly composts, bark and shavings, heather twigs) are the substances most often used as packing beds in biofilters. The aim of the study was to evaluate the rate of hydrogen sulfide removal in pine bark. The initial concentration of hydrogen sulfide was up to 58% v/v. The removal rates of this gas, using the pine bark bed, ranged from 0.003 $cm^3\ g^{-1}\ min^{-1}$ (115.64 $g\ m^{-3}\ h^{-1}$) to 0.040 $cm^3\ g^{-1}\ min^{-1}$ (1541.85 $g\ m^{-3}\ h^{-1}$). The results of a preliminary test suggest that the process is abiotic. In order to eliminate biotic pathways of hydrogen sulfide removal, the samples were sterilized.

1. INTRODUCTION

Biogas, produced during waste storing in landfills and wastewater treatment, contains, on an average, from 0.05 to 2.0% v/v of hydrogen sulfide (WOODCOCK and GOTTLIEB [14]). It originates as a result of anaerobic decay of sulfate and sulfur-containing organic substances. H_2S should be removed from the biogas for many reasons, especially for safety, but also in order to decrease the emission of sulfur oxides, which are formed when the biogas containing H_2S is combusted (TRUONG and ABATZOGLOU [12]). Desulfurization (removal of sulfur compounds) can be carried out in many ways, depending on several parameters, e.g. the composition of the biogas, its pressure and temperature. Biological methods of H_2S removal seem to be the most attractive in the process of biogas purification due to low investment costs (POTIVICHAYANON et al. [10]). The most popular biological methods are biofiltration, biotrickling filtration and bioscrubbing. Of these, biofiltration is used especially for odour elimination. Chemotrophic bacteria, e.g. *Thiobacillus, Thermothrix, Thiothrix* or *Beggiato*, are widely used for the biofiltration processes, especially for organic and

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inorganic sulfur compound oxidation. The *Thiobacillus* bacteria are most popular due to their ability to grow in an environment with oxygen deficiency and a low pH. Chemotrophs are microorganisms which derive the energy necessary for the synthesis of organic compounds from the oxidation of inorganic compounds, e.g. H_2S, and use inorganic carbon (CO_2) as a carbon source. When the process of hydrogen sulfide oxidation is conducted under aerobic conditions, oxygen is an electron acceptor; when the process occurs under conditions of oxygen deficiency, the other compounds act as electron acceptors (e.g. nitrate). The packing material of a biofilter is a basis for active biomass and often supplies it with nutrients necessary for growth (OYARZÚN et al. [8]). The impure gaseous stream passes through the biofilter, the packing material absorbs biodegradable compounds and microorganisms degrade the impurities into inert products as minerals, H_2O and CO_2 (VINCENT and HOBSON [13]). A good biofilter-supporting material ought to be characterized by high porosity, high water-holding capacity, adequate ability to adsorb malodorous gases, low cost, light weight, large specific surface area and large buffering capacity for acidic final products (HIRAI et al. [3]). The packing materials often used in biofiltration processes are soil, peat (MARTIN et al. [7]), heather twigs, bark chips (KURITA and KAMATA [5]), activated carbon (FANLO et al. [2], MALHAUTIER et al. [6]), sludge from wastewater treatment plant and compost (KNAUF [4]). Of these, compost is most often used for malodorous gas biofiltration, being easy to get and cheap. A high content and multiplicity of microorganisms, high water-holding capacity and high concentration of nutrients are its additional advantages (DELHOMENIE and HEITZ [1]).

After considering many earlier studies concerning hydrogen sulfide oxidation in the organic materials in the dynamic flow systems, it can be claimed that in most of them H_2S oxidation processes are regarded as occurring in a biological way.

In the first part of the study, in which bark was used, we evaluated the rate of H_2S removal in this material. The second stage of the experiment was conducted in order to check what type of the processes, biological or nonbiological, predominates in H_2S removal in bark. It was examined whether or not the bark sterilization (removal of the microorganisms) influences the removal rate of hydrogen sulfide. The values of this rate obtained in the experiment were compared with the results of earlier examinations (done on municipal waste compost and organic substrate POKON).

2. MATERIALS AND METHODS

2.1. DESCRIPTION OF THE EXPERIMENT

In order to achieve our aim, a static experiment was conducted, in which pine bark was used. The bark was taken from an odour removal biofilter placed in the "Hajdów"

Municipal Wastewater Treatment Plant near Lublin. The biofilter was used for purifying the stream of gases generated in the mechanical part of the plant. The biofilter had been working since 2005.

The gaseous hydrogen sulfide was produced from the concentrated liquid H_2SO_4 and sodium sulfide in Kipp's apparatus.

In the first part of the study, a gaseous hydrogen sulfide, whose initial headspace concentration ranged from 3 to 41% v/v, was injected into the vials. In the second part, this injection lasted until the concentration had reached 58% v/v. The hydrogen sulfide injection into the vials was conducted using a syringe. During the injection process, the second needle was brought in the caps to equalize the pressure within. The trials in the first part and in the second part of the study were conducted in two and three repetitions, respectively. The bark samples used for both parts of the experiment had not previously been inoculated with the H_2S-utilizing bacteria, but had been fed by supplying hydrogen sulfide in 10 cm^3 doses every day for 2 weeks before the experiment was started. In order to see whether H_2S can be adsorbed on glass, teflon or rubber, 3 vials without any material were used as control samples. H_2S in the same concentrations as those in the first part of the experiment was introduced to the vials. A time-dependent analysis of H_2S concentration in the vials showed that no sorption had taken place.

At the first stage of the study, ten glass vials, each 40 cm^3 in volume, containing 1-g bark samples were prepared. The vials were tightly closed with plastic caps with teflon-rubber coverings and incubated at the temperature of 22±2 °C in daylight.

At the second stage of the study, four series of vials (each of them in three repetitions) were prepared. 1-g bark samples were introduced into twelve glass vials, each 40 cm^3 in volume. The vials were closed with plastic caps with teflon-rubber coverings. Six of the vials were sterilized in a Samsung microwave M182DN by 600 W of power applied for 2 minutes. Next, all the vials were divided into four series, each consisting of three vials:

series I – sterilized vials, kept in daylight;

series II – nonsterilized vials incubated at the same temperature, placed also in daylight;

series III – sterilized vials, kept at the same temperature as before, but in complete darkness provided by a small cardboard container;

series IV – nonsterilized vials, incubated in darkness.

All the vials were incubated at the temperature of 22±2 °C.

2.2. ANALYTICAL METHODS

Gas samples of 150 µl volume were taken from the vials' headspace by a gas-tight syringe through the teflon-rubber part of the covering and analyzed chromatographically

(GC Shimadzu 14B), using a glass column filled with Porapak Q. In order to integrate the peaks, the CHROMA for Windows program (ChromaX 2007 version 1.0 b) was used. The rate of hydrogen sulfide removal (q) was determined as the amount of H_2S oxidised per unit of material volume during a unit of time, according to the equation:

$$q = \frac{\Delta C \cdot V}{\Delta t \cdot m}, \tag{1}$$

where:

q – the rate of H_2S removal ($cm^3 g^{-1} min^{-1}$);
ΔC – the change in hydrogen sulfide concentration between two measurements (%);
Δt – the unit of time (min);
m – the weight of the material (g);
V – the vial volume (ml).

A statistical analysis, using the *t*-Student test, was conducted. The critical values of t were measured and compared with those found in the tables at the level of significance $\alpha = 0.05$ and the proper degrees of freedom. Considering the decrease of the hydrogen sulfide concentration in 5 trials of the first part of the study, in two of them a statistically significant relationship was observed. It was also significant for the H_2S removal rate increasing with a hydrogen sulfide concentration increase. The same situation was observed in the case of a hydrogen sulfide concentration drop measured in MSW compost, POKON and in four series of bark in the second part of the study.

3. RESULTS AND DISCUSSION

A time-dependent decrease of the hydrogen sulfide concentration in the first stage of the study was observed in all vials containing bark samples, independently of the different initial H_2S concentration (figure 1). The rates of the hydrogen sulfide removal ranged from 0.005 $cm^3 g^{-1} min^{-1}$ (192.73 $g m^{-3} h^{-1}$) to 0.022 $cm^3 g^{-1} min^{-1}$ (848.02 $g m^{-3} h^{-1}$) (figure 2). These values can be compared with the corresponding values from our previous paper, where the rates of H_2S removal in municipal solid waste (MSW) compost and organic substratum POKON were determined (ZDEB et al. [16]). The decrease in H_2S concentration with time in those cases was also observed (figure 3). The rates of H_2S removal measured in the MSW compost ranged from 0.01 to 0.34 $cm^3 g^{-1} min^{-1}$ (from 569.8 to 19373.7 $g m^{-3} h^{-1}$), while for the organic base POKON they varied from 0.005 to 0.1 $cm^3 g^{-1} min^{-1}$ (from 196.9 to 3937.3 $g m^{-3} h^{-1}$), depending on an initial H_2S concentration (figure 4). As can be seen, many times higher rates of hydrogen sulfide removal were observed in the case of MSW compost, after comparing them with the equivalents determined in POKON and in bark. Removal of H_2S in bark was the slowest.

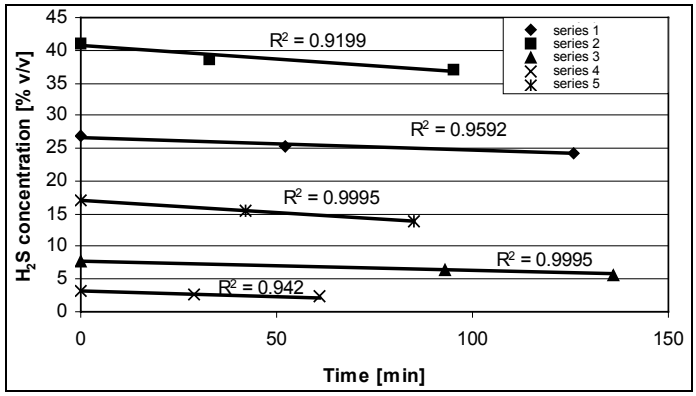

Fig. 1. H_2S concentration in bark from biofilter versus time

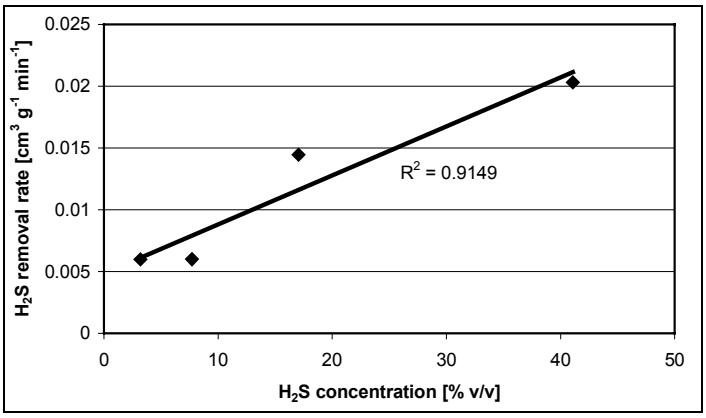

Fig. 2. Influence of H_2S concentration on rate H_2S removal in bark

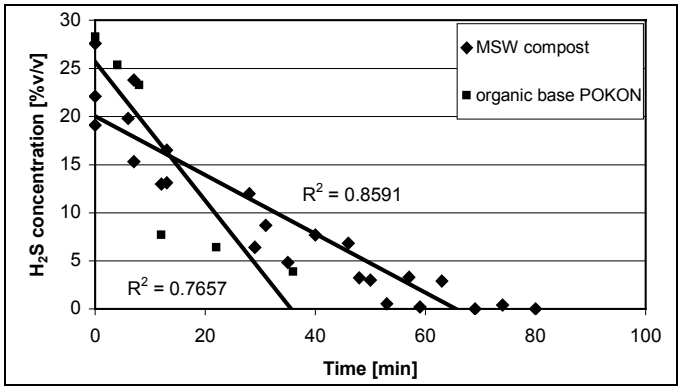

Fig. 3. H_2S concentration in municipal solid waste (MSW) compost and organic base POKON versus time (ZDEB et al. [16])

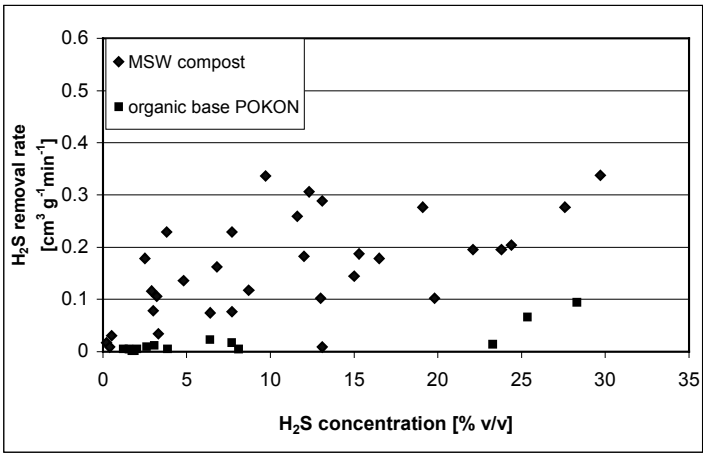

Fig. 4. Influence of H_2S concentration on rate of H_2S removal in municipal solid waste (MSW) compost and organic base POKON (ZDEB et al. [16])

As could be observed both in the case of bark and the remaining two materials (MSW compost and the organic base POKON), the rates of hydrogen sulfide removal became higher with the increase of H_2S initial concentration (figures 3 and 4). Complete substrate saturation was not observed in any of the organic materials under examination. This means that higher initial H_2S concentration will probably increase the rate of H_2S removal.

The initial phase of the hydrogen sulfide decomposition in all the cases was conducted under aerobic conditions and the second one, after oxygen depletion in the air inside the vials, in an anaerobic environment. The decrease in H_2S concentration was still observed even if the oxygen was not found in the headspaces. Therefore, it can be concluded that oxygen availability was not a limiting factor influencing the rate of H_2S removal. The mechanism of this process needs to be examined in the next stage of the studies, described in a further part of this paper.

The examination of the rates of H_2S removal in bark, MSW compost and organic base POKON was conducted under static conditions, thus the values obtained cannot be exactly compared with the values from the studies carried out in dynamic flow systems. The concentrations of hydrogen sulfide introduced into the vials were many times higher than those in the experiments carried out under dynamic conditions. There are some literature data which present the rates of H_2S removal, obtained in flow biofiltration systems packed with organic materials. PINETTE et al. [9] found the maximal rate of H_2S removal in the biofiter filled with compost, bark mulch and wood chips equal to 2.4 g m^{-3} h^{-1}. YANG and ALLEN [15] reported that the highest rate of hydrogen sulfide removal in a compost biofilter was equal to 130 g m^{-3} h^{-1} in a bench scale experiment. In turn, SERCU et al. [11] claimed that the maximum rate of H_2S removal measured in the biofilter filled with a mixture of MSW compost and dolomite was 28.5 g m^{-3} h^{-1}.

The results of the second stage of the examination aimed at explaining the process mechanisms are presented in figure 5. The decrease in the H_2S concentration with time in the headspaces was observed both in the sterilized and nonsterilized samples.

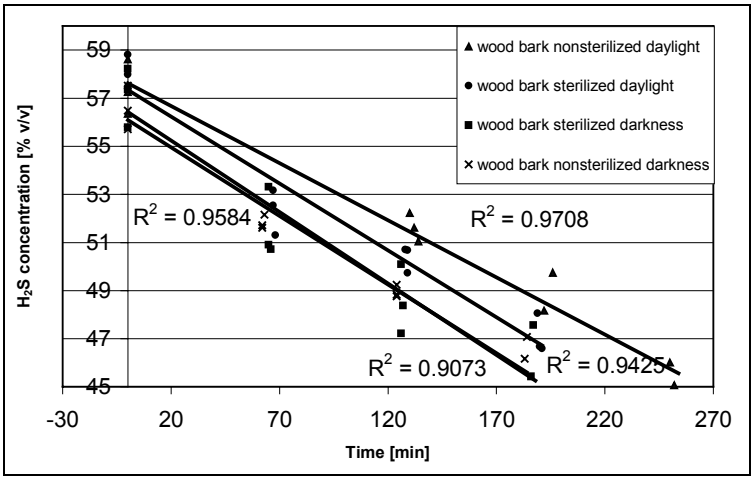

Fig. 5. H_2S concentration versus time
in bark samples incubated under various conditions

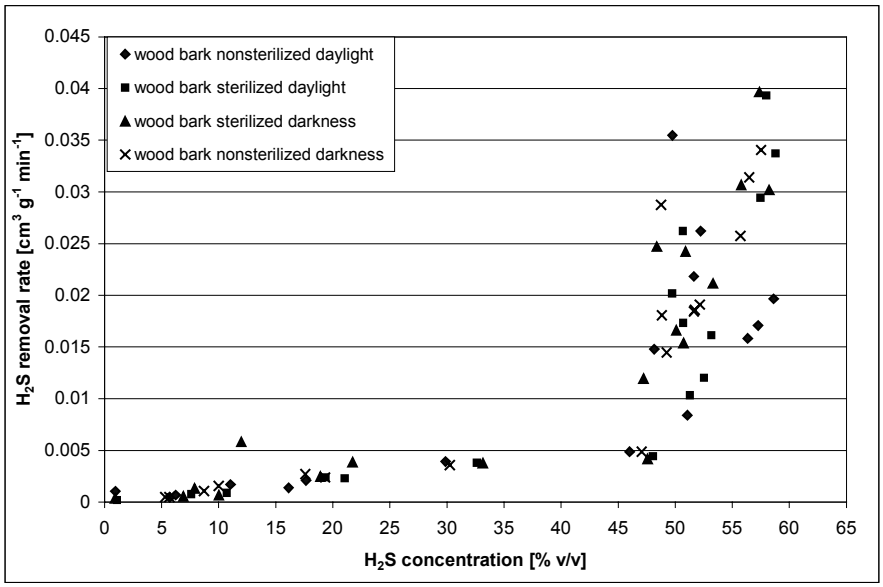

Fig. 6. Influence of H_2S concentration on rate of H_2S removal
in bark incubated under various conditions

In order to show what kind of relationship occurs, the rates of H_2S removal dependent on the hydrogen sulfide concentrations in these four series were compared graphically (figure 6).

Generally, it can be said that the rates of the hydrogen sulfide removal increased with the increase in H_2S concentration and in all four series were comparable. The minimum of rate H_2S removal in bark sterilized and incubated in daylight was 0.010 $cm^3 g^{-1} min^{-1}$, whereas its maximum value was 0.040 $cm^3 g^{-1} min^{-1}$. In the case of the series with nonsterilized samples incubated in daylight, the removal rates ranged from 0.008 $cm^3 g^{-1} min^{-1}$ to 0.035 $cm^3 g^{-1} min^{-1}$. For the sterilized series incubated in darkness, the following minimum and maximum rates of hydrogen sulfide removal were obtained: 0.012 and 0.040 $cm^3 g^{-1} min^{-1}$, respectively. The rates of hydrogen sulfide removal found in nonsterilized bark samples incubated in darkness ranged from 0.014 to 0.034 $cm^3 g^{-1} min^{-1}$. The results of these observations allow us to claim that elimination of microorganisms in bark samples does not inhibit the hydrogen sulfide removal. Thus it could be inferred that biological processes do not seem to be predominant in H_2S removal in bark samples. In view of that, other processes of different nature should be taken into account in H_2S removal, e.g. chemical processes such as reaction with heavy metals and precipitation of sulfides, or physicochemical processes such as sorption in organic matter.

4. CONCLUSIONS

The results of the experiment are controversial compared with the literature data which claim that the process of H_2S removal from the biogas in the bark biofilter has a biochemical character. We find that the process proceeds also after the bark sterilization, which suggests that non-biological transformations seem to predominate in the H_2S removal process. The rates of H_2S removal in the bark samples ranged from 0.003 $cm^3 g^{-1} min^{-1}$ (115.64 $g m^{-3} h^{-1}$) to 0.040 $cm^3 g^{-1} min^{-1}$ (1541.85 $g m^{-3} h^{-1}$), and their values depend on the initial concentration of hydrogen sulfide. No substrate saturation was observed in the range of H_2S concentration up to 58% v/v. The removal of H_2S was conducted both under aerobic conditions (when oxygen was present at the vials) and under anaerobic conditions (after oxygen depletion).

The problem of the nature of the H_2S removal is worth further examination, which will help to determine what process prevails in hydrogen sulfide removal in bark samples, a microbial or chemical one. The analysis of products and their pathways should also be conducted.

Bark seems to be the least effective material in hydrogen sulfide removal from all the materials studied here as the rates of H_2S removal were the lowest of all those obtained for the organic substances described in the paper.

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