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CLEANING OF H₂S FROM POLLUTED AIR USING PEAT BIOFILTER

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Abstract. Every year about 64 thousand tons of polluted air is being released to the ambient air. More than 30% of this pollution consists of toxic sulfur compounds. The properties of biological air cleaning technology – biofiltration with peat media – has been discussed in the article. Research was performed by using biofilter from Vilnius Gediminas technical university laboratory. During testing ambient air, polluted with sulfur dioxide, was pulled through the biomedia with division of *Thiobacillus* microorganisms and calculations of cleaning efficiency were performed. Was determined the efficiency of peat biofilter charge (changing the technical characteristics of the air flow rate, the number of layers, the pollutant concentration value) depending on the nature of the investigated sulfur compounds and their concentrations.

Keywords: hydrogen sulphide, biofilter, biofiltration process, peat media.

Introduction

The biggest concern of these times in both developed and developing countries is the rapid growth of industry and energy sectors, which cause growing emissions to the ambient air. 30% of this pollution consists of toxic for humans and environment sulfur compounds.

Ever since the beginning of the 20th century began the active interest in the biological air purification technology. This method makes it possible not only ecologically clean the polluted air environment, but also the construction of various construction equipment, whereas the load can be used inexpensive, multi-process resulting from the material – bark, rushes, straw, peat, activated sludge, etc.

Experimental investigation and assessment of the effectiveness of peat charge biodegradation sulfur compounds helps to make suggestions based on the design of efficient and cost-effective biofilters for different industries.

Meanwhile, sulfur hydrogen is emitted by many polluting enterprises. These companies include all of the chemical industries, where the H₂S gas is used as a raw material; as well as the industry, which is processing sulfide and other sulfur compounds, as they occur during the interim process or as a waste product. Equally important in the aspect of the formation of hydrogen sulphide in the air pollution dispersion terms are agriculture and food industries. Fermentation takes place in industrial processes and other organic substances in anaerobic decomposition, where

stands organic and inorganic sulfur-containing material (Chung et al., 2001, 2010; Hartikainen et al., 2000, 2011).

According to the data of earlier worldwide studies, as much as 90% hydrogen sulphide is released into the air with natural gas and only 10% H₂S emissions are anthropogenic in origin. Sulfur hydrogen concentration changes on the production of organic waste type. Hydrogen sulfide gas concentration depends on the origin of raw materials. It may vary from 0.1 to 2% of industrial waste and more than 3% of the protein containing manure or organic waste. The biggest source of hydrogen sulphide emissions is an oil refinery industries, crude oil processing/management companies, acid gas processing/storage management stations and transmission/pipelines. Besides H₂S is emitted into the air from animal fat and oil processing, waste treatment operations, blast furnaces, brewery and fermentation processes, chemical manufacturing processes: carbon disulfide, dyes, sulfur soap, polyethylene, rubber, plastics, rayon, synthetic fibers, cooling agents, glue, etc., fertilizer production, oily fish processing, abattoirs, sewage treatment plants, metal processing, leather tanning, asphalt storage and so on. Lithuania’s major source of emissions of hydrogen sulphide is PLLC *Orlen Lithuania*, oil refinery operating in Mažeikiai.

According to the order of Minister of Environment and Minister of Health (October 30th, 2000), concerning pollutants in quantities of ambient air are restricted by

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national criteria list and limit the air pollution values, in the table below are the allowable emissions of hydrogen sulphide in the ambient air limit of half an hour and an average of 24 hours (daily) time.

In the Table 1 of the said act is not provided the mean of air pollution 24-hour limit value of hydrogen sulphide. Half-hour limit value is applied for environmental impact assessment of air contamination. Average daily pollutant concentration is determined from at least four half-hour measurements of these pollutant concentrations carried out during the day at regular intervals.

Sulfur hydrogen gas is toxic and are environmentally hazardous, because during combustion hydrogen sulfur turns into sulfur dioxide that contributes to acid rain formation.

H₂S can be identified by smell. Odor sensing threshold 0.012–0.03 mg/m³. A slight, but clearly felt smell of H₂S concentration is 1.4–110 mg/m³. Relatively strong (used to it cannot feel) 3.3 mg/m³. Strong smell 7–11 mg/m³. The limit at the workplace: a long-term exposure limit 14 mg/m³, exceeded limit value – 20 mg/m³.

Table 1. Statutory hydrogen sulphide limit of ambient air pollution value

| Pollutant                  | The limit of ambient air pollution value, mg/m³ |
|----------------------------|-----------------------------------------------|
|                            | Half an our | The average 24-hour (daily) |
| Hydrogen sulphide (hydrogen sulfide) | 0.008 | – |

Hydrogen sulphide is a highly toxic substance that can accumulate in low areas and systems (e.g., sewers, animal farms and sewage pits), which can cause poisoning. According to the nature of performance H₂S inhibits the respiratory enzymes, blocking the oxidative enzyme activity in tissues of oxygen and causes hunger, irritation of the respiratory tract and mucous membranes and skin. May be caused vulnerable nervous system – may cause muscle pain, fingers, tongue, convulsions may develop psychotic, palms sweating. Acute poisoning by sulfur dioxide can cause death. Has negative impact on fauna. When hydrogen sulphide in stables is more than 1 mg/kg, it suddenly causes death to animals (Omri et al., 2011; Philip & De-shusses, 2003; Wang & Li, 2011; Vani et al., 2000).

Studies have also shown that this substance constitutes an adverse effect on vegetation. Excessive amounts of sulfur dioxide slows plant growth rate, can damage the leaves. In this case, the plants have difficulty to reset and occurs crop failure prognosis. However, it is found that small amounts of hydrogen sulphide can be used instead of sulfur fertilizer.

1. Methodology

The study was carried out with the biofilter, located in Vilnius Gediminas Technical University, Department of Environmental Protection laboratory. It was first performed with a peat biofilter packing efficiency of cleaning the hydrogen sulphide from the ambient air. All measurements of concentrations are made before and after the air pollution flow through the biofilter media.

The methodology for the determination of hydrogen sulphide (H₂S) concentrations in the ambient air testing air volume 80 dm³.

Concentration of hydrogen sulphide is produced by chemical reaction:

\[ \text{Na}_2S + H_2SO_4 \rightarrow H_2S + \text{Na}_2SO_4 \]  

One-hydrogen sulphide sampling conducted aspirators help. The absorption dishes, with added 5 ml of absorbent solution, dish ends are connected by plastic tubing that ends directed to the sampling points. In this way, air is pulled at different speeds for about 10 minutes. Sampling time absorbing containers should be protected from direct sunlight. Get samples suitable for the analysis of 24 hours of collection.

Absorbent container filled with the sample to 5 mL line with distilled water. The absorbent dish, add 1 ml of N, N-dimethyl-p-phenylenediamine and 1 drop of ferric chloride solution. Test tube samples are mixed and after ten minutes photoelectrocolorimeter measured by optical density at a wavelength of 670 nm. Cuvette wall thickness of 10 mm.

N, N-dimethyl-p-phenylenediamine (DFD) solution made by dissolving 100 mg of DFD 100 ml of sulfuric acid solution (1:1), which is produced in 100 ml of water slowly in small portions by pouring 100 ml of concentrated sulfuric acid, stirring constantly.

For catching the concentrations firstly was taken at least four contacted together absorbent dishes. In each has been added 10 ml of the absorbent solution. With the help of electroaspirator polluted air was pumped through absorption dishes with velocity of 2 dm³/min by pulling air 15–20 minutes.

After the absorption of concentration is finished the samples of liquid from absorbent dishes is taken into the measuring cylinders additionally adding 0.5 ml copper acetate solution of 0.05% and mixing all together. After 30–35 minutes optical density is measured with wavelength equal λ = 400nm. The absorption solution is made of 1.5% diethylamine solution.

In order to cultivate microorganisms in the charge for a month was maintained constant temperature (28 °C) and moisture regime (68%). Peat fraction size was chosen after analyzing the results of experiments performed in the world. Biological air cleaning efficiency can be influenced by the change of temperature (25–32 °C). Reduction of temperature (<25 °C) influences compaction of charge, decreased circulation flows and the gradual formation of a specific odor emitting anaerobic environment. Temperature is measured with a thermometer TPK during each experiment. The quality of cleaned air is assured by maintained humidity conditions (68%). In the absence of medium humidity (<68%) the degradation of organic
pollutants is less intensive as the living organisms can no longer eat, grow and multiply, they become inactive and after a certain amount of time can definitively die. Increasing humidity conditions (>68%) promotes the formation of anaerobic conditions and shortens biomedia operation. Biomedia moisture was determined during each experiment using psychrometer MV-4M.

The air flow velocity was measured in the biofilter during the experiments. It was performed by a device Testo 452 with a Pito tube after each layer of biologically active media. Each measurement was performed five times. Air flow velocity was calculated:

\[ w = 0.81r - 0.4951, \]

where: \( w \) – the true velocity of the air; m/s, \( r \) – instrument readings, m/s.

In order to choose an effective biomedia for biofilter, different fractions of peat charge were analyzed and their porosity was determined. These fractions include 10–30, 30–60 mm of peat samples.

During the experiments the overall mass of dry and wet peat charge was measured (scale precision 0.00005 g). Given that the peat cell density 625 kg/m³ (dry charge) and 673 kg/m³ (68% humidity) the volume of chosen fractions were measured. The peat charge sample was poured into 1000 ml volume cylinder. After that the cylinder was weighted to determine their bulk density \( \rho_p \), kg/m³. After the bulk density was measured the porosity of the given fraction wood waste charge sample was calculated using the formula below:

\[ P = 1 - \frac{\rho_D}{\rho_p} \cdot 100\%, \]

where: \( P \) – porosity, %; \( \rho_p \) – bulk density of peat charge, kg/m³; \( \rho_D \) – density of peat charge cells, kg/m³.

Air samples were taken in the breathing zone using electric aspirator, which is connected to the absorbent vessels. Air is pulled 5 minutes at 20 l/min.

Determination of the concentration of the sample was carried out using a spectrophotometer. Hydrogen sulphide concentrations in the ambient air (mg/m³) were calculated by the following formula:

\[ X = \frac{ab}{cV_0}, \]

where: \( a \) – hydrogen sulphide found in the analyzed volume, µg; \( b \) – the total volume of the sample, ml; \( c \) – volume of the sample taken for analysis, ml; \( V_0 \) – volume of the air taken for the analysis, l.

The concentrations of hydrogen sulphide in the ambient air, mg/m³, is the sum of the concentrations obtained by calculating the first and second absorbent dish samples:

\[ X = X_1 + X_2, \]

where: \( X_1 \) – hydrogen sulphide, found in the analyzed sample of first absorber (mg/m³); \( X_2 \) – hydrogen sulphide, found in the analyzed sample of second absorber (mg/m³).

The biofilter efficiency \( E, \) % was calculated after determining the hydrogen sulphide concentrations by photometric analysis:

\[ E = \frac{C_0 - C}{C} \cdot 100. \]

where: \( C_0 \) – hydrogen sulphide concentrations in the air before and after cleaning (mg/m³).

2. Results

After about 30–41 day-long biomedium activation before every experiment, gradually increasing the allowable hydrogen sulfide concentrations and changing the device operating mode (allowed air flow rate, the boot height, etc.) has been studied in biofilter efficiency.

The overall removal efficiency of hydrogen sulfide in biofilter packed with peat charge is shown in Figures 1 and 2. As mentioned before the pH value was kept approximately at neutral levels, so the same conditions are applied for hydrogen sulfide.

The measured porosity of this charge was equal to 52%. The above figure shows that the biofilter is effective at treating air stream from low concentrations of sulfur dioxide. The removal efficiency up to 94% was determined when treating the polluted air stream up to 30 mg/m³.

When determining the effectiveness of different fraction charge a dramatic drop in removal efficiency was seen (Figure 2).
In Figure 2 is shown the overall removal efficiency of hydrogen sulfide using bigger fraction peat charge has decreased from 94 to 87%. This result is given to the fact that the higher fraction has a bigger porosity value and therefore the contaminants are absorbs slower than compare to the smaller fraction peat charge.

In the experiment, the filter efficiency was tested depending on the number of its charge layers. The increase in the number of the layers from one to five resulted in higher efficiency of air cleaning due to greater amount of the biomedia and higher concentration of microorganisms. When the number of layers was increased up to five, efficiency of air cleaning at that same initial concentration was higher. Results of hydrogen sulfide removal efficiency depending on the layer height are given in Figures 3 and 4.

Injecting the air with lower concentration (from 5 to 29 mg/m³), the air cleaning efficiency after one layer and after five layers hardly differed (4–10%). For example, the efficiency of air cleaning of hydrogen sulfide with the initial concentration of 5 mg/m³ after one charge layer was 90%, after five layers it was 94%. With the increasing initial pollutant concentrations, biofiltration efficiency change after one and five layers reaches 5%.

Injecting the air with lower concentration (from 4 to 14 mg/m³), the air cleaning efficiency after one layer and after five layers differed 7–15% when using higher fraction peat charge (30–60 mm). With the increasing initial pollutant concentrations, biofiltration efficiency change after one and five layers reaches 9%.

Next experiment involved the determination of removal efficiency according to the air stream flow rate. During this experiment, the air polluted with hydrogen sulfide was injected at the speed ranging from 0.02 to 0.1 m/s. The results of this experiment are shown in Figures 5 and 6.

Figure 5 shows the results when measuring the efficiency of 10–30 mm fraction peat charge, which has porosity value of 52%. At the pH = 7 the filter efficiency of 92% is achieved when the speed of hydrogen sulfide with the initial concentration of 6 mg/m³ and flow rate of 0.02 m/s. Accordingly, when the initial concentration of hydrogen sulfide is up to 30 mg/m³, the air to be clean may be injected at the speed of 0.08 m/s and even at a higher speed, in which case the efficiency of air cleaning is 86%. If the speed of the airflow passing the filter is increased to 0.1 m/s without changing the above mentioned test conditions (the initial pollutant concentration 96 mg/m³, biofiltration efficiency goes down to 63%.

Figure 6 shows the results when measuring the efficiency of 30–60 mm fraction peat charge, which has porosity value of 76%. The filter efficiency of 90% is achieved when the speed of hydrogen sulfide with the initial concentration of 6 mg/m³ and flow rate of 0.02 m/s. If the speed
of the airflow passing the filter is increased to 0.1 m/s when test conditions are the initial pollutant concentration 94 mg/m³, biofiltration efficiency goes down to 64%.

Conclusions

1. Studies have shown that the efficiency of the filter, cleaning the air from hydrogen sulfide is highly dependent on allowable pollutant concentrations. Biofilter is best applicable for pollutants removal from polluted air stream when lower initial concentrations are present (6–30 mg/m³).

2. Biofilter air cleaning efficiency improves when reducing the air flow rate from 0.1 to 0.02 m/s (e.g. hydrogen sulfide treatment at air flow rate 0.02 m/s the removal efficiency initial concentration C = 15 mg/m³ is equal to E = 92%. When the velocity was increased to 0.10 m/s, the efficiency declined to 74%), as well as increasing the height of the charge (from 150 to 750 mm) and the number of layers (1 to 5).

3. Efficiency of the biofilter greatly depends on the fraction size of peat briquettes charge. Experiments showed that choosing smaller (10–30 mm fraction of peat), 15–20% improves in device efficiency because smaller fraction has larger surface area and the richer number of microorganisms.

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