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Section: Environmental protection

Research into Efficiency of Ammonia Removal from Polluted Air Using an Adsorber with Glauconite Packing Material

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Abstract

In recent decades climate change caused by human economic activities has been a matter of growing concern worldwide. Waste production and management resulting from intensified human activities is one of they core environmental problems. Generated waste can be used for the recovery of biogas; however, another problem arises – undesirable pollutant emissions from biogas. In a biogas recovery alternative, pollutants, such as hydrogen sulphide (H_2S) and ammonia (NH_3), make an adverse impact on equipment causing its corrosion. During experimental tests with biodegradable waste the amount of ammonia released in bioreactors was recorded. Adsorbents of a natural origin – glauconite and zeolite – were used for biogas purification. When the initial ammonia concentration was 24.2 mg/m^3, the efficiency of purification using glauconite packing material reached 93.0%, while when the pollutant's initial concentration stood at 24.0 mg/m^3 zeolite packing material produced a cleaning efficiency of 77.4%.

Keywords: Biogas; glauconite; adsorption; ammonia.

1. Introduction

Human activities are inevitably related to waste generation and therefore society's increasing needs lead to increasing consumption levels resulting in waste production. Biogas can be produced from easily degradable organic raw materials and wastes (animal manure, waste from slaughter-houses, dairy farms, breweries or distilleries), which offers an opportunity to replace exhaustible fossil fuel resources by renewable resources. The recovery of biogas from production, agricultural, municipal and other organic wastes helps avoid additional waste utilisation costs related to transportation or landfilling. Biogas is a combustible mixture of different gases which is released when microorganisms degrade, aerobically or anaerobically, materials during the process of decaying. This gas is composed of different gases most of which are methane (CH_4), carbon dioxide (CO_2), hydrogen sulphide (H_2S), ammonia (NH_3) and hydrogen (H_2) gas (Table 1) [3].

Table 1. Composition of biogas [3]

Substance	Symbol	Precentage
Methane	CH_4	50–70
Carbon Dioxide	CO_2	30–40
Hydrogen	H_2	5–10
Ammonia	NH_3	~<1
Hydrigen Sulphide	H_2S	~2

An increasingly growing interest in biogas production increases the amount of knowledge about the processes of biogas production optimisation aimed at creating a useful product by using solid municipal waste the amounts of which are excessively large; however, there arises another problem concerning the use of generated biogas – it is necessary to remove impurities from biogas, such as hydrogen sulphide and ammonia [6]. These impurities in biogas adversely affect equipment and cause corrosion. Hydrogen sulphide gas is dangerous because of the formation of dioxide during its burning. However, while burning ammonia forms nitrogen monoxide which is likely to increase environmental pollution from power plants [5].

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1.1. Biogas generation

Anaerobic digestion is a natural process of degradation by which organic materials are split into simpler compounds. Anaerobic microorganisms break down organic materials in the absence of oxygen, which results in the discharge of by-products – methane, carbon dioxide and other gases.

During biodegradation of organic materials in a reactor all groups of microorganisms work in concert so that intermediary products released by one group are used by other groups of microorganisms. Bacteria producing biogas require an appropriate medium for the maintenance of their vital functions [16].

In order to obtain an appropriate distribution of organic materials during anaerobic treatment several conditions and factors are required. It is necessary to control the operational parameters of equipment in order to intensify microorganism activity and enhance the efficiency of anaerobic digestion. The main factors responsible for biogas generation are the following:

- content of dry matter;
- temperature;
- pH;
- carbon/nitrogen ratio;
- mixing [11].

Mixing in an anaerobic bioreactor results in a better contact between microorganisms and substrate and also in an increased capacity of bacteria populations to get nutrients for degradation. Mixing and anaerobic treatment materials have to be mixed before the process of digestion in order to ensure adequate homogeneity. It is necessary to create all conditions for maintaining microorganism activities [4, 11].

1.2. Biogas purification technologies

Biogas contains aggressive and hazardous impurities which have to be removed in order to increase the durability of gas-fired facilities and of the entire biogas system [12]. Seeking to improve the quality of biogas it is necessary to remove hydrogen sulphide, ammonia and similar admixtures. For this purpose various physical and chemical techniques and means are used. Their choice and application depend on the composition and concentration of impurities in biogas, the method of biogas use and related requirements. Normally, a larger content of impurities is permitted when biogas is used in water boilers, and a very small one in the case of internal combustion engines. Considering that ammonia is soluble in water its concentration in biogas can be reduced using frozen water vapour removal techniques and any water purification technologies by which biogas is transferred through a reverse water flow [5]. Prior to that ammonia gas can be dried and cooled in order to achieve its better solubility in water. Although the simplest biogas purification technique is physical absorption using water, this process consumes very large amounts of water [10] and absorbs only a low percentage of ammonia.

One of the most efficient methods for the removal of gaseous pollutants is adsorptive air purification. Adsorptive air cleaning methods help to efficiently remove even lowest concentrations of gaseous pollutants. An adsorptive gas purification technique is based on the use of the physical properties of certain solids with an ultra microscopic structure making it possible to segregate separate components from a gaseous mixture and retain them on their surface.

Environmentally, it is useful to abandon the purification of biogas using chemical sorbents and substances whose inputs in the cleaning process are very large. Alternatively, sorption of chemical impurities can be performed using appropriate indigenous sorption minerals.

2. Research methodologies

2.1. Methodology for research into anaerobically treated biogas

The aim of the work is to analyse the quantity and composition of produced biogas using biodegradable waste of fine and coarse fractions. Anaerobic treatment tests were performed using a batch bioreactor. Biomass was supplied to the batch bioreactor via a special opening and was discharged through the same opening at the end of the experiment.

In order to maintain biomass temperature batch bioreactors were placed into a special vessel with water where 30±1 °C temperature was maintained by heating elements. The pH of substrate was determined before and after the experiment. To measure the gas amount it is necessary to have a gas accumulation vessel of 0.0045 m^3, a vessel with water, nozzles for hose fixing, hoses and a ruler. The amount of accumulated gas is determined using the formula (1):

$$Q = \frac{\pi \cdot d^2}{4} \cdot h , \tag{1}$$

Here: d – gas storage tank diameter (PVC tube), m ; h – gas storage tanks, pumping head, m.

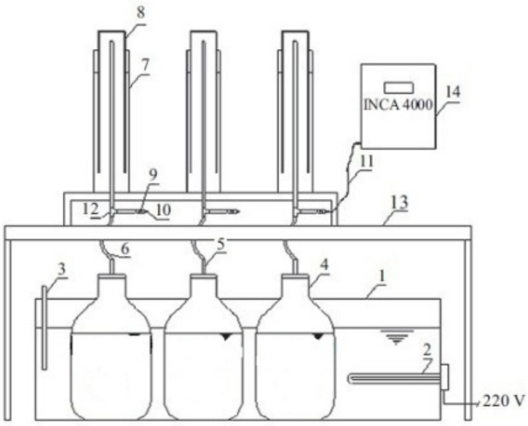


Fig. 1. A scheme of the laboratory bench bioreactor: 1 – container with water; 2 – water heating element; 3 – thermometer; 4 – bioreactor; 5 – hose connector, a sturdy; 6 – flexible tube; 7 –container with of water; 8 – gas storage capacity (PVC pipe); 9 – valves; 10 – connector for gas to exit; 11 – flexible hose; 12 – tee; 13 – table; 14 – gas analyzer [9]

The biogas accumulation vessel is connected by an elastic hose with a biogas analyser. The measurement of biogas composition lasts for 9 minutes. When the measurement time is over, the device shows the average values of biogas components.

The parameters of biogas amount and composition are recorded on a daily basis.

2.2 Adsorption research methodology

The aim of experiments is to determine the efficiency of ammonia removal from biogas using glauconite packing material in an adsorber as well as the possibilities of using glauconite.Experiments on ammonia adsorption were carried out using a developed experimental biogas purification adsorber (Fig. 2) filled with adsorbing materials.

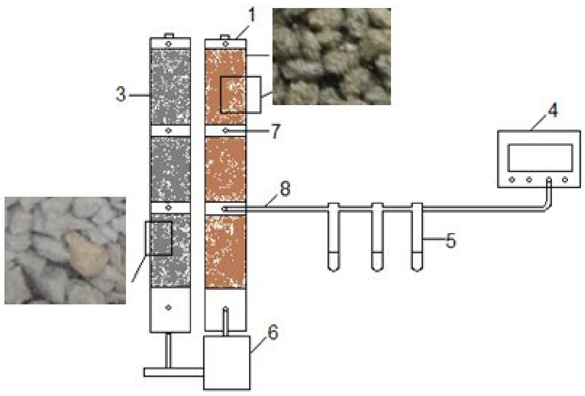


Fig. 2. Stand equipment for ammonia adsorption analysis: adsorber housing filled with adsorbing materials; glauconite packing material; zeolite packing material; aspirator; sorption tubes; gas accumulation bag; biogas sampling places; connecting hoses.

The main filter element of adsorber structure – filter material composed of glauconite, 0.6 mm in diameter, and of zeolite granules. Zeolite packing material is used for the comparison with experimental results.

A test stand consists of a plastic housing of the adsorber which is 0.15 m in diameter and 0.50 m high. The adsorber is divided into three sections in order to maintain a uniform airflow distribution within the entire layer of the packing material. Each section is separated by metal sieves from each other.

Each section is filled with a layer of packing material, 0.1 m thick. Sampling openings, 0.08 m each, are fitted up under each section and tightly closed with removable plugs.

Biogas is connected to the bottom part of the adsorber, while adsorption tubes filled with 0.01N HCl solution are connected to measurement point 1. Experiments are conducted in all three measurement points. Gas is supplied via a layer of the packing material and adsorption tubes by the aspirator. The efficiency of adsorber's filter material is analysed in all measurement points by maintaining a uniform suction rate of 0.06 m/s. After determining the gas suction rate in the aspirator, gas is supplied vertically upward for 10 minutes via the adsorber's sections and the content of ammonia is measured in all points. Measurements completed, the solution is poured from adsorbers into separate test-tubes. 3 ml of the sample and 2 ml of distilled water are taken for analysis. Nessler's reagent, 0.5 ml, is added to the obtained solution and stirred. The optical density of the solution is measured after 5 minutes by a spectrometer at a wavelength of 450 mn. The concentration of ammonia is calculated using the formula (2):

$$c = \frac{c_1 \cdot V_1}{V_2 \cdot Q \cdot t \cdot K}, \text{ mg/m}^3 \quad (2)$$

Here: c – ammonia concentration, mg/m^3; c_1 – ammonia concentration in the sample according to a calibration curve, µg/ml; V_1 – sample volume in the adsorption vessel, ml; V_2 – sample volume taken for analysis, ml; Q – sucked airflow rate, l/min; t – suction rate, min; K – coefficient for concentration conversion into normal conditions.

The obtained results for glauconite efficiency are compared with results for zeolite.

3. Research results

3.1. Equations and formulae

Experiments for the determination of biogas yield and composition were carried out in cooperation between the scientists of the Environmental Protection Institute (EPI) and the Environmental Protection Department (EPD) of Vilnius Gediminas Technical University. One of the most important indicators of efficiency in anaerobic biodegradable waste treatment is the amount of produced biogas. These experimental tests particularly focused on the composition of biogas [9]. The experiment used biodegradable waste of fine and coarse fractions. It was determined from the obtained biogas that fine–fraction mixed municipal waste has a higher energy potential. Subsequent tests use biogas recovered from municipal waste of fine fractions. Figure 3 shows the composition of biogas measured in three different bioreactors.

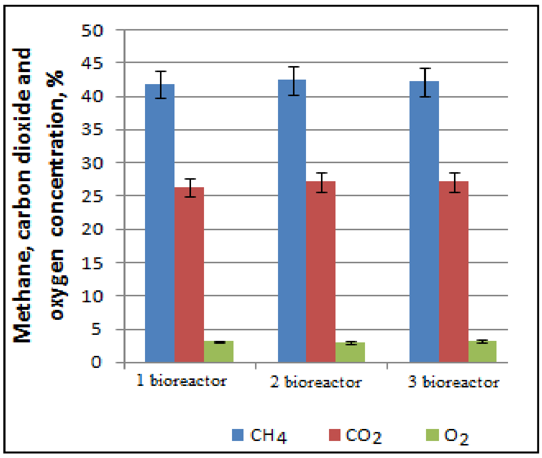
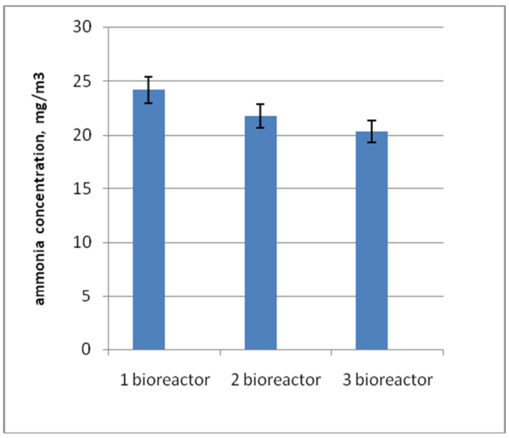
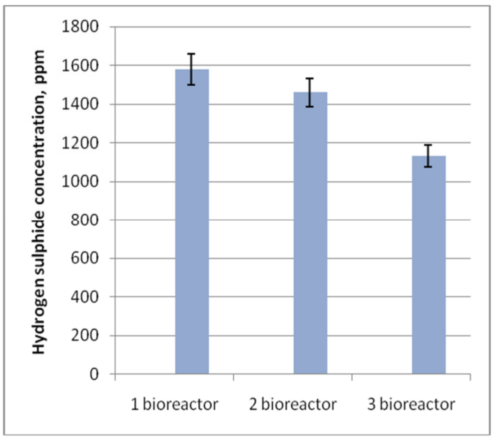


Fig. 3. Methane, carbon dioxide and oxygen concentration in biogas

The content of methane in biogas ranged between 41.5% and 44.8%, that of carbon dioxide – 25.2% and 28.1%, while the concentration of oxygen in biogas nearly did not change. When the concentration of oxygen rises above 5%, methane release in biogas is poor. From the viewpoint of anaerobic digestion, a biomass is evaluated by the content of fats, proteins and carbohydrates. The yield of biogas and methane content in it depends on the ratios between these substances. A substrate with a larger content of carbohydrates determines a more rapid production of biogas because carbohydrates are easier to decompose, while the concentration of methane in biogas can reach 50% [1, 9]. Different substrates result in different biogas yield and composition [7]. Figure 4 shows the amounts of the pollutants concerned in released biogas.



a)



b)

Fig. 4. Ammonia concentration in biogas (a), mg/m^3 and hydroge sulphide concentration in biogas (b)

The analysis of the amounts of other components in biogas shows large quantities of hydrogen sulphide and ammonia and it is therefore necessary to find an alternative for the removal of these pollutants. The amount of H_2S varied from 1131 to 1580, while the amount of ammonia was in the range of 20.36 and 24.2 mg/m^3. The pH of substrate of both fractions was also measured before and after the experiment.

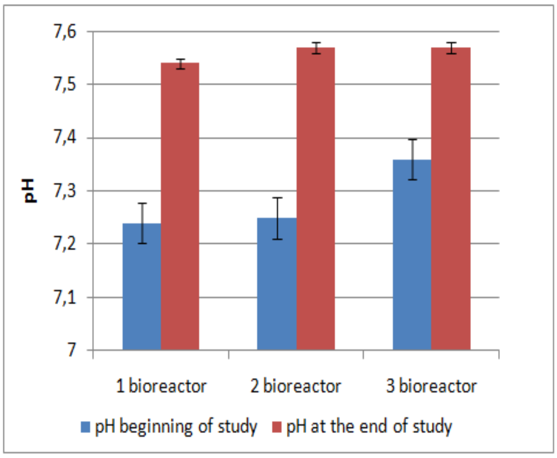
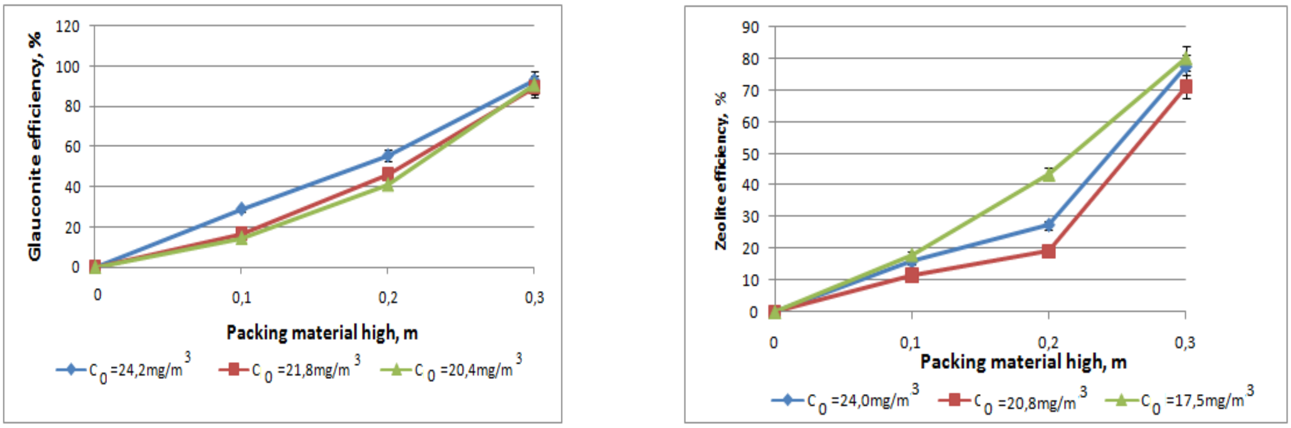


Fig. 5. Substrate pH in the beginning of study and at the end of study

Figure 5 shows pH results obtained during three experimental tests with fine-fraction mixed municipal waste. As the figure shows, the pH indicator reached 7.24 during the first test, 7.25 during the second and 7.36 during the third test. The pH was also determined after the tests which reached 7.54, 7.57 and 7.57, respectively. According to the scientific literature, the optimum pH of substrate should be weakly alkaline – pH 7–8 [2].

3.2. Adsorption research results

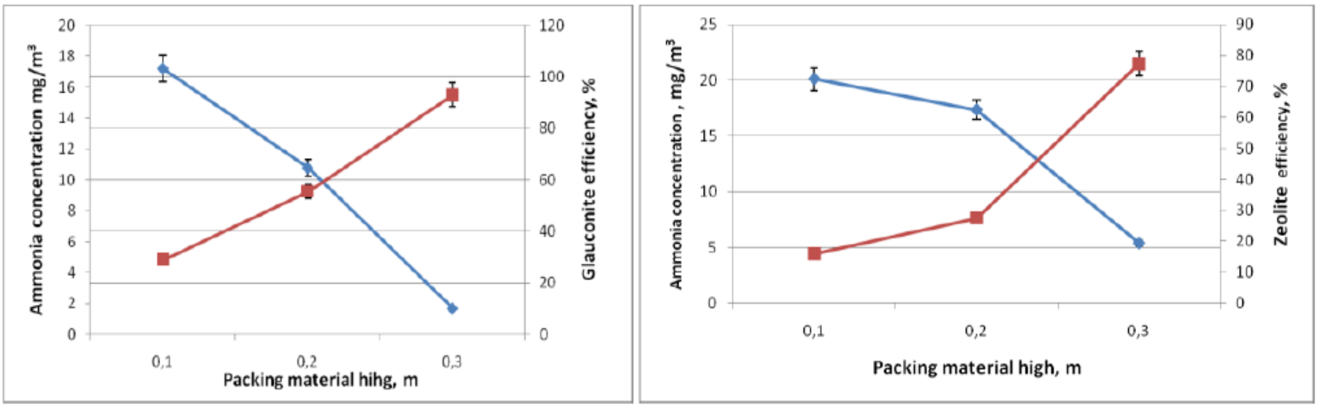
In order to evaluate and compare the efficiency of natural adsorbents in removing ammonia, experiments were conducted using different concentrations of ammonia. This experiment used two adsorbents – glauconite and zeolite. Glauconite packing material is a natural mineral of the silicate class that is absolutely non-toxic. Glauconites, unlike zeolites, have a layered molecular structure and therefore they have a larger active surface area. Figure 6 shows the dependence of the efficiency of glauconite and zeolite on different heights of packing materials when the concentration of ammonia is different.



a) b)

Fig. 6. Glauconite (a) and zeolite (b) efficiency dependence for different boot heights and different ammonia concentrations

It is easy to notice a significant increase in efficiency in both glauconite and zeolite packing material after biogas has passed through them at a height of 20 cm in both adsorbents. The purification of biogas using zeolite was widely analysed by Spanish scientists when zeolite granules were activated through their heating and calcination. The efficiency of purification achieved during experiments reached 91.3%. The comparison of the results of this experiment with the scientists experiments has shown that the efficiency of non-activated zeolite is lower by a mere 11.1%. The use of glauconite for biogas purification has been scantly analysed. Research into glauconite efficiency could be useful in terms of future prospects. Below is analysed biogas containing the highest concentrations of ammonia. Figure 7 shows the dependence of the highest concentration of ammonia on the efficiency of different adsorbents.



a) b)

Fig 7. Glauconite (a) and zeolite (b) efficiency at the highest concentration of ammonium

It follows from the comparison of the obtained results that glauconite is more efficient than the other adsorbents. When the concentration of ammonia is the highest the purification efficiency of glauconite reaches 93.0%, while that of zeolite – 77.4%. Zeolite does not have a high ammonia sorption capacity, i.e. using glauconite the concentration of ammonia dropped from 24.2 mg/m^3 to 1.7 mg/m^3, whereas in the case of zeolite it fell from 24.0 mg/m^3 to 5.4 mg/m^3. Glauconite produced a 16% higher efficiency than zeolite.

4. Conclusions

1. It has been determined during experimental tests on the degradation of mixed municipal waste of fine and coarse fractions that fine–fraction municipal waste has a higher energy potential. Therefore, this type of waste was used for further research into biogas purification.
2. The content of methane in biogas ranged between 41.5% and 44.8%, that of carbon dioxide – 25.2% and 28.1%, while the concentration of oxygen in biogas nearly did not change. When the concentration of oxygen rises above 5%, methane release in biogas is poor.
3. It follows from the performed analysis of the amounts of undesirable pollutants in biogas that the released amounts of hydrogen sulphide vary between 1131 and 1580 ppm, whereas the concentration of ammonia in biogas ranges between 20.4 mg/m^3 and 24.2 mg/m^3. When the concentration of pollutants is large they should be removed applying alternative techniques in order to protect equipment against corrosion.
4. Natural minerals – glauconite and zeolite – were used for biogas purification. Since these minerals are found in Lithuania they are a prospective means of biogas purification. It has been determined during the application of these adsorbents for ammonia removal from biogas that glauconite enjoys a higher sorption capacity. When the initial ammonia concentration is 24.2 mg/m^3 the efficiency of purification reaches 93.0%; meanwhile in the case of zeolite, when the initial concentration of ammonia is 24.0 mg/m^3, efficiency represents 77.4%.

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