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An Efficiency of H_2S Removal from Biogas via Physicochemical and Biological Methods – a Case Study

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1. Introduction

One of the main challenges of modern world is to supply sufficient amount of energy. Fossil fuels not only that are running out very quickly, but also their combustion causes emission of CO_2 to atmosphere, which can create threat of climate warming (Lindzen 2010; Hoedl, 2011; Udo and Pawłowski, 2011; Pawłowski, 2012). Because of that, more attention is paid nowadays to renewable sources of energy, using which not only decrease fossil fuels use but also reduce CO_2 emission. One of the most interesting, among many conceptions, is waste-to-energy approach, in particular using sewage sludge for different kinds of energy production (Piecuch, 2000; Montusiewicz et al., 2008; Cao and Shan, 2012). During sewage sludge anaerobic digestion there is biogas produced. Its composition depends on the sort of feedstock, its moisture, process temperature, pressure and on a fermentation stage. The content of hydrogen sulfide in biogas depends mainly on the type of fermented substrate (Deublein and Steinhauser, 2008).In order to improve the biogas caloric value and make it economical to compress and transport the undesirable components like CO_2, H_2S and H_2O should be removed. It is possible to remove H_2S by precipitation practically unsoluble metal sulfides (Pawłowska and Pawłowski, 2007).

Hydrogen sulfide removal process can be conduct in many ways, which depend on several parameters, i.e. the composition of the impure gas, its pressure and temperature, sort and concentration of pollutants. Physical and chemical methods are regarded as less efficient because of high operating costs and high chemicals prices. Moreover, there are problems with byproducts of reactions disposal. The advantages of biological processes are low required capitals and absence of negative effects on atmosphere. One of the main factors influencing the biological process efficiency is temperature. Effective removal of most odours occurs in temperature range 20–40^{o}C (Bohn, 1992; Yang and Allen, 1994; Zdeb and Pawłowska, 2009). In case of hydrogen sulfide, sometimes it is difficult to define what kind of elimination process occurs. The problem of H_2S removal process nature was studied in few articles, but still is worth further examinations (Pawłowska et al., 2009). Suming up, biological methods seems to be the most attractive from other methods of odours removal.

The wastewater treatment plant “Hajdów”near Lublin (Poland) is a mechanically-biological unit with an average daily flow about 60 000 m^3/day. It produces 100 tons of mechanically dewatered sludge per day. The sewage sludge digestion is conducted at anaerobic digestors (each with a volume of 8 270 m^3). As a result of a fermentation process, biogas containing some amounts of hydrogen sulfide is produced.

The aim of this paper was to compare the efficiency of H_2S removal from biogas conducted on the bog iron ore and in biological desulfurization station placed at the wastewater treatment plant “Hajdów”.

2. Materials and methods

2.1. Characteristic of biological desulfurization station

In order to achieve an aim of the study, the data of 8 months’ time measurements conducted on the biological desulfurization station at the wastewater treatment plant “Hajdów” were analyzed. The station, working as a biotrickling filter for hydrogen sulfide removal, was examined in order to evaluate its desulfurization efficiency. A scheme of the station is presented in Fig. 1. The desulfurization installation replaced a bog iron ore, which was removed especially because of economical reasons. The raw bog iron ore costs and problems with spent material disposal were the most important negative factors resulted in such a decision.

The measurements began when currently working setup started to operate, that is at the end of June 2008.

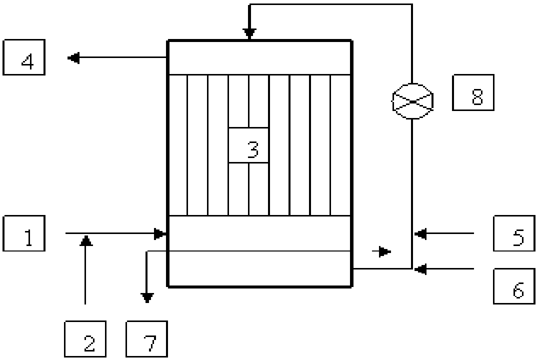


Fig. 1. Scheme of desulfurization station designed and constructed by AAT Abwasser und Abfalltechnik GmbH: 1 – biogas contaminated with hydrogen sulfide, 2 – air stream, 3 – desulfurization tower, 4 – H_2S free biogas, 5 – process water, 6 – supernatant, 7 – flushing liquid, 8 – heat exchanger (AAT-Biogas Technology)
Rys. 1. Schemat stacji desulfuryzacji zaprojektowanej i wykonanej przez AAT AbwasserundAbfalltechnik GmbH: 1 – biogaz zanieczyszczony siarkowodorem, 2 – strumień powietrza, 3 – wieża odsiarczalni, 4 – biogaz pozbawiony siarkowodoru, 5 – woda procesowa, 6 – roztwór płuczący, 7 – popłuczyny, 8 – wymiennik ciepła (AAT-Biogas Technology)

The desulfurization tower (95 m^3 volume) is made of polypropylene and filled with commercially available pall rings. Plastic pall rings serve as a large surface area basis for microbial growth and immobilization. The sulfur-oxidizing bacteria *Thiobacillus* (*thiooxidans and thioparus*) and *Sulfolobus*, are responsible for the biological hydrogen sulfide oxidation. There are extra media supplied to improve the H_2S decomposition. The supernatant solution and small amount of fresh water (process water) are added mainly to flush the pall rings from sulfur and to provide the adequate moisture, pH and supply for the bacteria. The nutrients solution for the bacteria in a mineral fertilizer form is supplied continuously during day. Moreover, the nutrients solution is used as a pH level buffering factor. Warm water is lead to the system as a source of heat in order to maintain operating temperature on required level (28 to 32°C). The flushing liquid is brought in order to wash out H_2S oxidation end-products. The oxygen, necessary for the microorganisms, is supplied by use of an air blower.

2.2. Process description

Biogas at the wastewater treatment plant “Hajdów” is produced mainly at sewage sludge fermentation process conducted in the anaerobic digesters. The biogas from the digesters is then brought to the biological desulfurization station, presented in Fig. 1. The station characteristic and biogas required parameters are shown in Table 1. The setup operates at the average temperature about 29.6°C and pH 1.7. Its task is to reduce the concentration of H_2S in biogas to the value below 55 ppm, which is required in order to prevent the damage of metal elements of the biogas thermal utilization unit.

Table 1. The biological desulfurization installation characteristic and required biogas parameters
Tabela 1. Charakterystyka biologicznej odsiarczalni oraz wymagane parametry oczyszczanego biogazu

Parameter	Unit	Value
Installation		
Biogas flow rate	m^3/h	300–825
Maximum static pressure	mbar	40
Maximum underpressure	mbar	12
Temperature	°C	25–40
Relative humidity	%	100
Dust concentration in gas	mg/m^3	<5
Maximum gas pressure	mbar	40
Biogas		
O_2 concentration	% vol.	0–1
H_2S concentration	ppm	≤ 3000
NH_3 concentration	ppm	<20
H_2 concentration	% vol.	<1
CO_2 concentration	% vol.	<40
CH_4 concentration	% vol.	55–80

The raw biogas stream, contaminated with H_2S, is dosed with a controlled stream of air inside the desulfurization tower. The O_2 concentration is permanently measured to avoid explosive mixture of oxygen and methane ($O_2 < 5\%$ vol. of biogas). The input stream is supplied to the tower from the bottom and flows upward the filling. Inside the tower H_2S is absorbed and undergoes into liquid form (HS^-), which favours the oxidation process conducting by microorganisms (Fig. 2).

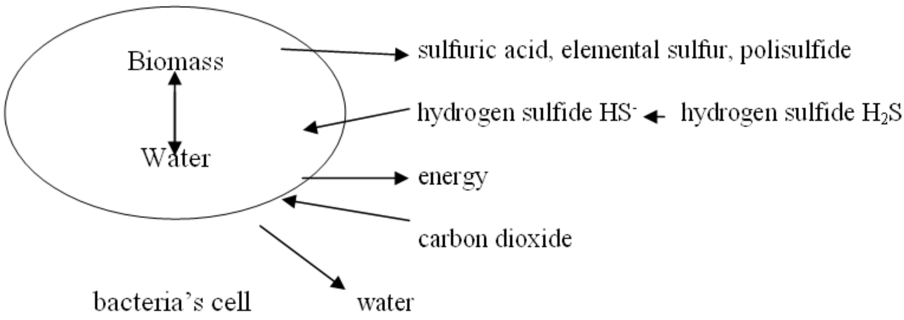


Fig. 2. Biochemical way of H_2S removal from biogas using microorganisms
Rys. 2. Schemat biochemicznego usuwania H_2S z biogazu
przez mikroorganizmy

Bacteria as a suspension are supplied in countercurrent to gas flow. Microorganisms are immobilized on pall rings, which constitute the packing material. The main end-products of H_2S oxidation process are sulfates (approx. 25% of products – Equation 1.1) and elemental sulfur (approx. 75% – Equation 1.2). A type of end-product depends on oxygen accessibility(AAT-Biogas Technology).

$$H_2S + 2O_2 \rightarrow H_2SO_4 \qquad (1.1)$$

$$2H_2S + O_2 \rightarrow 2S + 2H_2O \qquad (1.2)$$

Next, the hydrogen sulfide oxidation products are washed out from the filling bed by the flush water. The solution containing the reaction end-products is then recycled at the wastewater treatment plant influent.

After the removal of hydrogen sulfide and moisture, the biogas is ready to be used as an energy source. Desulfurized biogas is used mainly at the "Hajdów" wastewater treatment plant area. It serves as an energy source in heat and power plant (combined heat and power system) and is applied in dewatered sludge drying station. The biogas surplus is used by nearby factory producing blacktops and asphalt.

The data concerning the efficiency of H_2S removal from biogas by use the bog iron ore were obtained from the administrator of the wastewater treatment plant “Hajdów”. While the bog iron ore were using for biogas desulfurization, 180 tons of the waste ore were produced each year.

2.3. Analytical methods

The hydrogen sulfide concentrations were measured in the biogas entering and leaving the desulfurization station. The Draeger short term gas detection tubes type CH 29101 with lead acetate was used to determine H_2S concentration in raw biogas. The Gas Analyzer SSM 6000 (Pronova Analysentechnik) was applied for determination of the hydrogen sulfide concentration level in the stream of desulfurized biogas. Qualitative differences between measured values were the basis for the calculation of H_2S removal efficiencies, according to the equation:

$$E = \frac{C_1 - C_2}{C_1} \cdot 100[\%] \quad (1.3)$$

where:

E – hydrogen sulfide removal efficiency,
C_1 – H_2S in raw biogas concentration,
C_2 – H_2S in desulfurized biogas concentration.

3. Results and discussion

The biological desulfurization station has started to operate in June 2008. Before this data bog iron ore was used for the biogas desulphurization (data originating from two first quarters). Comparison of the results of biogas treatment processes conducted on the bog iron ore and in biological desulfurization station in 2008 is presented in Table 2.

Comparison of H_2S removal efficiencies (calculated on the base of data showed in Table 2) in particular quarters of 2008 allows to state, that the highest efficiencies were obtained in III and IV quarters. The values were 97.6 and 99.5%, respectively. The values calculated for I and II quarters were 75.1 and 89.9% respectively. It means, that biological desulfurization station with pall rings is more effective in hydrogen sulfide removal from biogas, than the previously working bog iron ore. The average values of H_2S removal efficiencies for the bog iron ore and biological desulfurization station were 82.5 and 98.6%, respectively. The average hydrogen sulfide removal efficiency obtained in currently working desulfurization station was about 16% higher than on bog iron ore.

Table 2. Concentrations of hydrogen sulfide, before and after the desulfurization process measured in 2008 (average values for particular quarters)
Tabela 2. Stężenia H_2S w strumieniu biogazu przed i po procesie odsiarczania mierzone w 2008 roku (wartości średnie dla poszczególnych kwartałów)

Quarter	Concentration of H_2S in biogas (ppm)	
	before the process	after the process
I (bog iron ore)	1110	276.0
II (bog iron ore)	980	99.3
III (biological desulfurization station)	800	19.3
IV (biological desulfurization station)	670	3.3

The values of hydrogen sulfide concentration levels and desulfurization efficiencies obtained in the desulfurization station in particular months of the measurements are shown in Table 3 and in Fig. 3.The average H_2S concentration introduced into desulfurization station was 751 ppm (±85 ppm).

Table 3. The average values of hydrogen sulfide concentrations in biogas stream, before and after the biological desulfurization station (average values for particular months)
Tabela 3. Średnie stężenia H_2S w strumieniu biogazu wchodzącego i opuszczającego stację odsiarczania metodą biologiczną (wartości średnie dla poszczególnych miesięcy)

Month	Concentration of H_2S in biogas (ppm)	
	before the process	after the process
July 2008	800	20.2
August 2008	800	14.0
September 2008	800	23.8
October 2008	607	1.0
November 2008	600	1.8
December 2008	800	2.5
January 2009	800	2.8
February 2009	800	0.4

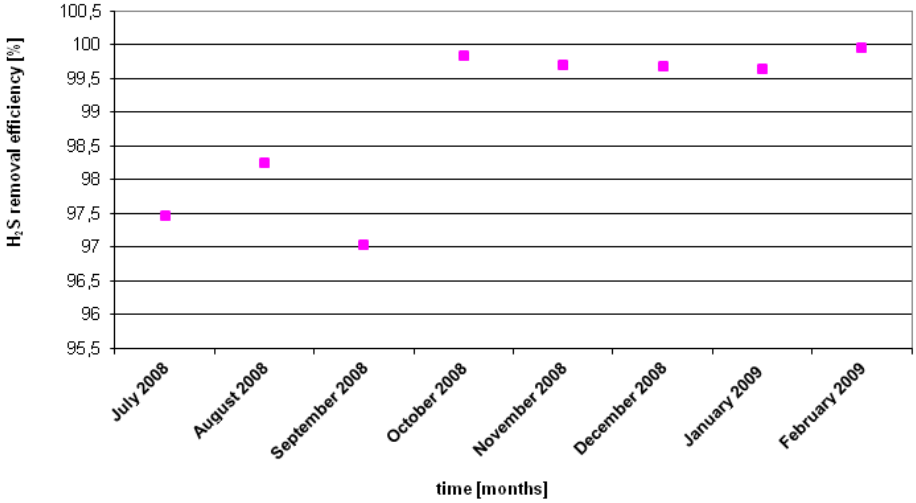
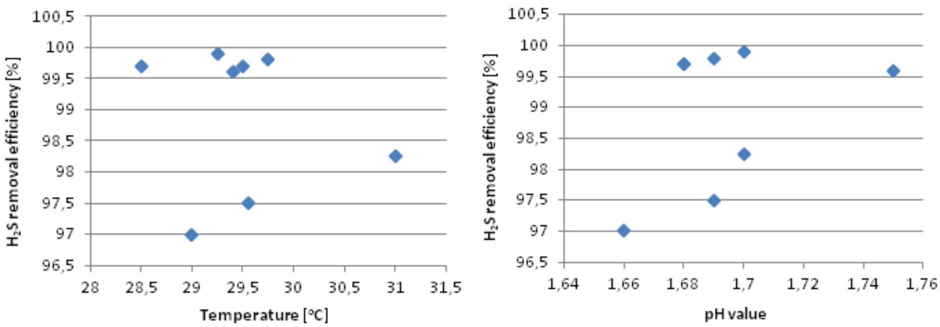


Fig. 3. Average H_2S removal efficiencies in a biological desulfurization station (data for the particular months of the measurement period)
Rys. 3. Średnie efektywności usuwania H_2S w biologicznej odsiarczalni biogazu (dane dla poszczególnych miesięcy, w których prowadzono pomiary)

The values of hydrogen sulfide removal efficiencies in a period of 8 months' time measurements ranged from 97.0 to 99.4%. The lower values were observed in the first three months of the station work. It probably resulted from adaptation of the microorganisms to operating conditions of the process.

Considering the relationship between H_2S removal efficiency from biogas and pH value, measured in flushing liquid and temperature inside the tower, it was stated that there were no significant dependences between these parameters (Fig. 4). The lack of the relationships may be explained by the narrow range of the variability of pH and temperature values during the observation period. Temperatures varied from 28.5 to 31.0°C, and pH values varied from 1.66 to 1.75. These values were in the optimum range for hydrogen sulfur oxidizing bacteria used in the desulfurization station.

The obtained hydrogen sulfide removal efficiencies may be compared with the efficiencies from other wastewater treatment plants with desulfurization units. However, it is difficult to find these information, because administrators unwillingly give it out. The wastewater treatment plant Skarżysko-Kamienna makes known, that its desulfurization station with bog iron ore reduces H_2S concentration in biogas from the level about 2800–5600 to the values below 140 ppm. So, its hydrogen sulfide removal efficiency is higher than 95% (www.skarzysko.org/modules.php?name=Content&file).



a) b)

Fig. 4. Relation between H_2S removal efficiency and temperature inside the tower (a) and for pH level of flushing liquid (b) measured in biological desulfurization station

Rys. 4. Efektywności usuwania H_2S w biologicznej odsiarczalni biogazu w zależności od temperatury wewnątrz stacji (a) oraz odczynu cieczy płuczącej (b)

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In a wastewater pretreatment plant of the Tyskie Brovarium there is a THIOPAQ system for biogas desulfurization used. The system bases on biochemical H_2S oxidation to elemental sulfur, as a main end-product. The obtained hydrogen sulfide removal efficiency is higher than 99% (www.veoliawaterst.pl/vwst-poland/ressources/documents/1).

Also the result of laboratory experiments found in the relevant literature showed the high efficiency of hydrogen sulfide removal conducted in biotrickling filters. Gabriel and Deshusses (2003) were studied a few reduced sulfur compounds removal efficiencies using a biotrickling filter with polyurethane foam inoculated with *Thiobacillus*sp. H_2S removal efficiency at an inlet concentration of 30 ppmv was 98%. This filter had an ability to remove other sulfur compounds, with the efficiency, as follows: carbon disulfide – 35%, carbonyl sulfide – 44% and methyl mercaptan – 67%, at the inlet concentrations of 70, 193 and 67 ppbv, respectively. Sercu et al. (2005) used a biotrickling filter with 1 L-polyethylene rings inoculated with *Acidithiobacillusthiooxidans* ATCC-19377 for hydrogen sulfide removal. The process was conducted at the inlet H_2S concentrations in the range from 400 to 2000 ppm. Neither low pH (2–3) nor change in operational conditions negatively influences the removal process run. The maximal removal efficiency of the hydrogen sulfide obtained in the experiment reached 100%. Soreanu et al. (2005) studied the H_2S removal under anaerobic conditions. Polypropylene balls inoculated with anaerobically digested sludge were used as a filter bed. Sodium sulfite in the nutritive solution acted as an oxygen scavenging agent, while nitrate, in the absence of oxygen, was used to function as an electron acceptor. At the H_2S inlet concentration of 500 ppm removal efficiency higher than 85% were achieved. When a nitrate solution was used as the only nitrogen/nutrient source, trace amounts of O_2 were the factor negatively influencing the microbial activity.

4. Conclusions

Taking into account the results gained from 8 months' time measurements, it was found that both: bog iron ore and biological desulfurization station with pall rings were effective in H_2S from biogas removal. The average value of hydrogen sulfide removal efficiency for the bog iron ore was 82.5%, whereas for biological desulfurization station: 98.6%. Thus, the average hydrogen sulfide removal efficiency obtained in currently working biological desulfurization station was about 16% higher than obtained on bog iron ore. It means, that biological desulfurization station seems to be more effective in hydrogen sulfide from biogas removal than the previously working bog iron ore. No significant relationships between H_2S removal and pH value, as also as between H_2S removal and temperature were observed.

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Efektywność usuwania H_2S z biogazu metodą fizykochemiczną i biologiczną

Abstrakt

Celem pracy było porównanie dwóch instalacji w aspekcie oceny ich efektywności w usuwaniu siarkowodoru z biogazu powstałego na skutek fermentacji osadów ściekowych w oczyszczalni ścieków „Hajdów" w Lublinie. W pracy zwrócono uwagę na coraz większe zainteresowanie odnawialnymi źródłami energii, użycie których powoduje zmniejszenie zużywania paliw kopalnianych. Stosowanie źródeł odnawialnych nie powoduje zanieczyszczenia atmosfery ditlenkiem węgla, emitowanym wskutek procesów spalania. Podczas beztlenowego rozkładu osadów ściekowych powstaje biogaz, czyli mieszanina głównie metanu, ditlenku węgla oraz gazów śladowych. Jednym z mikrozanieczyszczeń występującym w biogazie jest siarkowodór (H_2S). Siarkowodór jest gazem bezbarwnym i palnym, bardzo toksycznym i niebezpiecznym dla organizmów żywych.

Usuwanie siarkowodoru z biogazu prowadzone jest głównie ze względów zdrowotnych, ale zapobiega także korozji materiałów i zanieczyszczeniu atmosfery oraz wpływa na wzrost wartości kalorycznej biogazu. Wiele jest sposobów prowadzenia odsiarczania. O wyborze procesu decydują głównie skład gazu, jego temperatura oraz ciśnienie. Do usuwania siarkowodoru stosowane są metody fizyczne, chemiczne i biologiczne. Wadą metod fizycznych, chemicz-

nych i biochemicznych są wysokie koszty inwestycyjne i eksploatacyjne, wysokie koszty niezbędnych środków chemicznych oraz problemy z zagospodarowaniem odpadów. Najbardziej atrakcyjnymi wydają się być metody biologiczne, które charakteryzują się niskimi nakładami kapitałowymi oraz brakiem negatywnego wpływu na środowisko.

Mechaniczno-biologiczna oczyszczalnia ścieków komunalnych „Hajdów" w Lublinie charakteryzuje się średnim dobowym przepływem ścieków na poziomie około 60000 m^3/d. Powstaje tam 100 ton mechanicznie odwodnionego osadu dziennie. Wynikiem jego beztlenowego rozkładu jest powstający biogaz, wymagający odsiarczenia.

W pracy porównano skuteczności usuwania siarkowodoru z biogazu na złożu rudy darniowej oraz w biologicznej stacji odsiarczania firmy AAT (AbwasserundAbfalltechnik GmbH). Biologiczna stacja odsiarczania zastąpiła rudę darniowa, którą usunięto w czerwcu 2008 r. ze względu na wysokie koszty jej zakupu oraz duże ilości odpadów powstających przy jej wymianie. Dane dotyczące efektywności usuwania H_2S z biogazu na rudzie darniowej udostępnione zostały przez administratora oczyszczalni "Hajdów". Na skutek reakcji siarkowodoru ze związkami żelaza na rudzie darniowej wytrącały się siarczki żelaza. Na skutek tego, konieczne było częste wymienianie rudy, czego wynikiem były wysokie koszty eksploatacyjne i problem z zagospodarowaniem odpadów. Dane dotyczące skuteczności odsiarczania biogazu w odsiarczalni biologicznej zebrano z okresu ośmiu miesięcy pomiarów. Biologiczna stacja odsiarczania składa się z wysokiego zbiornika wypełnionego plastikowymi pierścieniami, stanowiącymi bazę dla rozwoju mikroorganizmów utleniających siarkę. Skuteczności usuwania siarkowodoru z biogazu wyliczano z różnicy jego stężenia przed wejściem na stację odsiarczania i po wyjściu ze stacji.

Stwierdzono, że obie metody (fizykochemiczna i biologiczna) są skuteczne w odsiarczaniu biogazu. Średnia skuteczność usuwania siarkowodoru z biogazu na rudzie darniowej wyniosła 82.5%, podczas gdy w biologicznej stacji odsiarczania: 98.6%. W aktualnie pracującej stacji odsiarczania skuteczność usuwania H_2S była wyższa o 16% w stosunku do skuteczności odsiarczania na rudzie darniowej. W okresie ośmiomiesięcznych pomiarów prowadzonych w biologicznej stacji odsiarczania nie stwierdzono wpływu pH i temperatury na skuteczność usuwania siarkowodoru z biogazu.