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PRACTICAL METHODS OF CLEANING BIOGAS FROM HYDROGEN SULPHIDE. PART 1. APPLICATION OF SOLID SORBENTS

Abstract

Hydrogen sulphide is a commonly occurring component of biogas that causes atmospheric pollution and corrosion of equipment used in biogas plants. Its removal before further processing of biogas is therefore necessary for environmental and technical reasons. The paper presents a critical review of technologies that use solid sorbents. The next paper will discuss the chemical and biochemical processes taking place in liquid systems.

Key words

Biogas, hydrogen sulphide removal, solid sorbents, fermentation, bioenergy

Introduction

Renewable energy sources (RES) have an increasing share within the energy balance of the European Union [1-5]. Although the agricultural biogas production sector is supported by the authorities and is of great economic importance, the document adopted by the government in July 2010, *"Directions for the development of agricultural biogas plants in Poland 2010-2020,"* is not sufficient, and investments in the agricultural biogas sector require even stronger financial support [5-8]. According to EU plans, in 2020 the share of energy from renewable sources of energy as part of total energy should reach at least 15%. Among these, technologies based on the conversion of biomass to biogas are important and are used mainly for the production of electricity or heat [6-29].

Biogas is a gas mixture consisting primarily of methane (CH_4) and carbon dioxide (CO_2), produced by methane fermentation as a result of controlled biological decomposition of organic matter in anaerobic conditions with appropriate microorganisms. In addition to the above-mentioned components, biogas contains small amounts of: hydrogen sulphide (H_2S), nitrogen (N_2), hydrogen (H_2), ammonia (NH_3), carbon monoxide (CO) and oxygen (O_2). The content of individual components in biogas is not constant, as shown in Table 1, depending on the technological process used and the type of feedstock used for biogas production [9, 7, 16, 20, 21]. The material subjected to methane fermentation can be either a vegetable substrate [6, 8-10, 20-25], an animal substrate [13, 19], brewing or distilling dregs and waste [2], sewage sludge [9, 11, 12, 14, 18, 20 22], or mixtures of these [10, 20-25]. The methane content of biogas determines its calorific value, e.g. the combustion of 65% methane biogas generates about 23 MJ/m^3 of heat [20].

Table 1. Percentage of main biogas components [20]

Biogas component	Component content	
	Range (%)	Average (%)
Methane	52-85	65
Carbon dioxide	14-48	34.8
Hydrogen sulfide	0.08-5.5	0.2
Hydrogen	0-5	trace substance
Carbon monoxide	0-2.1	trace substance
Nitrogen	0.6-7.5	trace substance
Oxygen	0.1	trace substance

Source: Głodek E. (red.), Pozyskiwanie i energetyczne wykorzystanie biogazu rolniczego. Wydawnictwo Instytut Śląski Sp. z o. o., Opole 2007

The content of hydrogen sulphide in biogas is usually small, but it should be removed since it is a cause of environmental pollution and problems with the operation of the plant. The remaining ingredients in trace amounts do not cause such great problems as hydrogen sulphide, which is generated at the acidogenesis stage of the methane fermentation process. The aim of the publication series is to present a guide to the most important methods for the removal of hydrogen sulphide from biogas, with the emphasis on simple, low-cost and relatively effective technologies, and thus likely to be widely used.

Hydrogen sulphide is a product of the decomposition of sulphur-containing compounds, including, but not limited to, amino acids (cysteine and methionine), sulphoxides, and sulphonic acids. It is also formed during the biological reduction of sulphates present in the fermented raw material. Hydrogen sulphide is a hazard, since, together with the water that is also in biogas, it forms corrosive condensate, destroying biogas plants' equipment and devices [15, 22]. In addition, it should be borne in mind that during the combustion process of biogas contaminated with hydrogen sulphide, sulphur dioxide will be formed by the following reaction:

$$H_2S + 1{,}5O_2 \rightarrow SO_2 + H_2O$$

Then the compound is gradually oxidized in the atmosphere to sulphur trioxide, a highly hazardous pollutant to the environment, because sulphuric acid is produced by the absorption of water, which in turn is one of the components causing the formation of acid rain [15, 22].

Biogas is most often used for the production of electricity and heat in cogeneration units. For this purpose, it is necessary to carry out a desulphurization and dehumidification process (removal of other unnecessary components is not economically viable). According to the literature recommendations, the concentration of hydrogen sulphide in biogas intended for combustion should not be higher than 1000 ppm. This value secures biogas combustion and heat recovery equipment against corrosion [15, 20, 22], and also reduces atmospheric pollution by the acid products of oxidation of hydrogen sulphide. According to Kujawski, in accordance with the recommendations of manufacturers of cogeneration equipment, biogas cannot have more hydrogen sulphide than 200-300 ppm [23]. On the other hand, Cebula and Sołtys indicate the following ranges of permissible H_2S content: power boilers up to 1000 ppm, internal combustion engines 50-100 ppm, gas injection into network 4-7 ppm and fuel cells below 1 ppm [24]. The injection of biogas into the gas network comes with the need to lower the concentration of hydrogen sulphide to concentrations below 10 ppm [25] or even below 1 ppm [22]. In this case, and in the use of biogas as fuel for motor vehicles, it is also necessary to remove other than H_2S impurities accompanying methane. Biogas is then subjected to processes that ensure sufficient drying, removal of carbon dioxide, nitrogen and chlorine compounds, as well as organic silicon compounds, according to national requirements [26].

Biogas can also be catalytically converted with steam, in order to produce synthesis gas rich in hydrogen, and useful, for example, in the production of methanol [20, 22]. Biogas desulphurization methods differ from natural gas desulphurization methods. The removal of hydrogen sulphide from biogas should be as simple as possible, preferably covering only one stage, with high efficiency under normal pressure and temperature conditions. In addition, the reagents should be selected so that they can be used, for example, as fertilizers.

Removing hydrogen sulphide using hydrated iron oxides, sodden ore and bauxites

The industrial methods of chemical desulphurization of biogas include the adsorption of sulphur compounds (primarily H_2S) on hydrated ferric oxide [15, 18, 22].

The adsorption process is efficient if the adsorbent has a significant specific surface area and is maintained at a sufficiently low temperature. Irreversible adsorption has the characteristics of chemisorption. Then the binding energy of the molecules on the surface of the adsorbent is so great that the adsorbate can be desorbed only as a chemical compound, even in the form of a solid [28-30].

Two forms of iron oxide have good efficiency of biogas desulphurization, i.e. crystalline iron oxide hydrates: α-$Fe_2O_3 \cdot H_2O$ and γ-$Fe_2O_3 \cdot H_2O$. They react easily with hydrogen sulphide and the process of their regeneration is practically complete [22, 31-34]. Fe_3O_4 ($Fe_2O_3 \cdot FeO$) oxide has a lower hydrogen sulphide adsorption capacity compared with the two forms of iron oxide above. In the process of hydrogen sulphide adsorption on the surface of hydrated iron (III) oxide, iron (III) sulphide is produced, according to the reaction [31]:

$$Fe_2O_3 + 3H_2S \rightarrow Fe_2S_3 + 3H_2O$$

If mercaptans are found in the purified biogas, they react as follows [22]:

$$Fe_2O_3 + 6RSH \rightarrow 2Fe(RS)_3 + 3H_2O$$

The optimum temperature for this process is about 38°C, while the reaction medium should be slightly alkaline and should amount to 8.0-8.5. In addition, the content of crystalline water in the adsorbent mass is important. If the pH of the purifying mass is lower and the temperature is higher (50°C), the resulting iron (III) sulphide loses the bonded water and forms a mixture of FeS_2 and Fe_8S_9 , then iron (II) sulphate and sulphur are created, which do not adsorb hydrogen sulphide, and they are not able to easily regenerate to iron (III) oxide [22].

In theory, one kilogram of hydrated iron (III) oxide is capable of absorbing 0.64 kilograms of hydrogen sulphide. In practice, however, the efficiency of this process is about 90%. After the adsorption capacity of the bed is exhausted, it is regenerated [22, 32, 34]. The resulting Fe_2S_3 reacts with oxygen from the air to produce iron (III) oxide and sulphur (S^{2-}) oxidizes to elemental sulphur (S^o), according to the reaction:

$$2Fe_2S_3 + 3O_2 \rightarrow 2Fe_2O_3 + 6S$$

Both processes: adsorption and regeneration of the bed can be repeated many times until the formation of elemental sulphur does not cover the active iron oxide surface and does not fill the space between its grains. In order for the adsorption and regeneration processes to take place simultaneously, a certain amount of air or oxygen can be added to the treated biogas. Both processes produce large amounts of heat, which hinder the execution, because excessive temperature increase of the adsorbent will cause loss of water and reduced H_2S bonding capacity. The resulting elemental sulphur can be removed by combustion. Sulphur (IV) oxide is formed, which can be used to produce sulphuric acid. Both oxides used for hydrogen sulphide adsorption are obtained from iron ores or metallic iron (about 75% iron (III) oxide, 10% water and other additives that come from iron ores) [20-22, 32].

Another popular adsorbent for the removal of hydrogen sulphide is sodden ore. The main component of the ore is crystalline limonite $Fe_2O_3 \cdot nH_2O$. Sodden ore is brownish porous sedimentary rock formed by the action of bacteria from soluble iron compounds in water. It can be most often found in areas where groundwater is near the surface of the soil, at a depth of about 30 cm, i.e. in river valleys, marshy areas or peat bogs. In Poland, the ore is found in Wielkopolska, Mazovia, Podlasie, Roztocze and Małopolska. The composition of sodden ore results from the conditions in which it was created. In addition to iron (III) oxide, small amounts of the following metal oxides may be detected: calcium, magnesium, potassium, sodium, iron (II), aluminum, titanium, as well as organic matter and water. The most effective are sodden ores containing from 45 to 55% iron oxide on the dry substance of the adsorbent, from 45 to 55% water in the cleaning mass, and a weight loss as a result of roasting about 30% [22, 32]. Fig. 1 below shows the ground module of the H_2S removal plant from biogas produced from sewage sludge in Rawskie Wodociągi i Kanalizacja Sp. z o.o. in Żydomice (RAWiK).

Fig. 1. View of the aboveground construction of the biogas desulphurization system using sodden ore at the Rawskie Wodociągi i Kanalizacja Sp. z o.o. company in Żydomice. Ownership of authors.

In a period of nearly six years, the composition of biogas was tested before and after its purification using sodden ore from the deposit in Strzyżów near Kalisz [32]. Biogas was generated by the fermentation of sewage sludge produced in the sewage treatment plant in two Separated Fermentation Chambers. The biogas purification process was carried out in a desulphurizer containing four layers of desulphurization bed based on sodden ore, modified by the introduction of activators and scavengers. The desulphurized biogas was stored in a tank, from which it was progressively sent via a measuring and distributing node to the boiler room and generators. In case of excess biogas, it was also burned in a torch. Biogas directed to the generators was further purified in adsorber filled with activated carbon and on a non-woven filter. Fumes were cooled in the heat exchanger and their unburnt components, such as carbon monoxide, were oxygenated with a catalytic converter [28].

Apart from ores obtained in Poland, examples of commercial adsorbents can be found on the market and in scientific literature. These include, among others: Sulfatreat 410-HP, containing iron oxides for the desulphurization and deodorization of gases at atmospheric pressure, as well as Sulfa-Bind from ADI International and Sulfur-Gte from GTP-Merichem [22, 35].

The sludge from the processing and purification of bauxite in the process of aluminum production is also suitable for the purification of biogas from hydrogen sulphide. Bauxite is a sedimentary rock that consists mainly of aluminum hydroxides. In addition, it also contains clay minerals, silica, oxides and iron hydroxides. This sludge has a high adsorption capacity, as demonstrated by studies carried out by Vietnamese and Japanese researchers [31], as the removal efficiency of hydrogen sulphide was 94.7%. Fresh sludge has better biogas removal efficiency than biodegradable sludge, so it is advisable to use only fresh material to make the process cost-effective and efficient. The advantage of this material is also its low price.

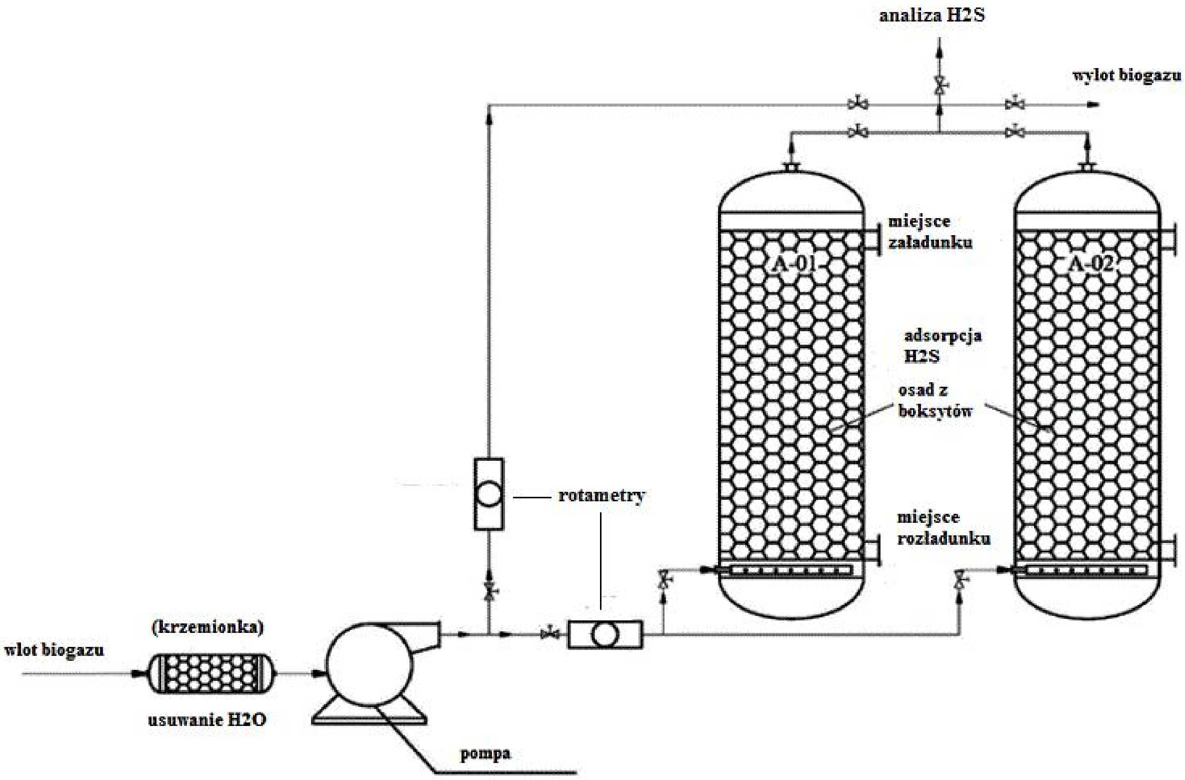

Fig. 1. Scheme of apparatus for the removal of hydrogen sulphide using bauxite sorbent [31]

Source: Q. Huynh, V. Q. Q. Thieu, T. P. Dinh, , S. Akiyoshi, Removal of hydrogen sulfide (H_2S) from biogas by adsorption method, 8th Biomass Asia Workshop, November 29-December 1, 2011, Hanoi, Vietnam.

A schematic diagram of a plant for the removal of hydrogen sulphide from biogas using bauxite sludge was proposed. The installation shown in Figure 1 was 95% efficient, with the purification of 20 m^3 per day of biogas with a content of up to 2500 ppm hydrogen sulphide [31]. The main part of the apparatus consisted of two columns for adsorption of hydrogen sulphide.

Oxidation of hydrogen sulphide in the gas phase with active carbon, molecular sieves and silica

Another method used for the desulphurization of biogas is the oxidation of hydrogen sulphide in the gas phase on activated carbon deposit, one of the oldest and most popular adsorbents [20-22, 30, 33-43].

As a result of reactions that occur on the surface of active carbon, hydrogen sulphide is catalytically oxidized, mainly to elemental sulphur, or to a lesser degree sulphur dioxide, which can in turn oxidize to trioxide (SO_3). In order for this process to take place, the presence of water and oxygen in the purified gas is necessary. Water, due to accumulation and condensation, forms a thin film that covers the hydrophobic surface of micro- and mesopores of the adsorbent. Oxygen diffuses through the water layer, then dissociates and adsorbs on the carbon surface. Hydrogen sulphide also diffuses into water, and if the pH of the environment is greater than 5, it also begins to dissociate [22, 34].

Unmodified activated carbon has a low sorption capacity relative to hydrogen sulphide, usually at the level of 0.02 g H_2S/g of active carbon. This sorbent, however, can be used for purifying gases that contain several ppm of hydrogen sulphide. Papres [22, 34] describes commercially available activated carbons with different degrees of physicochemical treatment, including:

- WVA-1100, from the company Westvaco, with a specific surface of 1700 m^2/g, made of wood and activated with orthophosphoric acid;
- Maxsorb, from the company Kansai, with a specific surface area of 2240 m^2/g, formed from the residue from the distillation of crude oil and activated with potassium hydroxide;
- Xtrusorb, from the company Calgon Carbon, with a specific surface area of about 1040 m^2/g, obtained on rock base using steam activation.

Modified activated carbons are more often used for the purification of biogas from hydrogen sulphide: much more efficient in the process of adsorption of hydrogen sulphide. Modification involves the introduction of basic nitrogen-containing groups into the sorbent structure (carbon monoxide or ammonia), basic oxides (MgO, CaO), hydroxides (NaOH, KOH) or sodium and potassium carbonates. Crystalline oxides of basic character, in this case MgO and CaO, exhibit little H_2S reactivity at room temperature, and low water solubility. They react with carbon dioxide, which is found in both air and biogas, to form bicarbonates and calcium carbonates or magnesium carbonates, present in the active carbon structure as separate phases. These compounds dissociate in contact with water and increase the pH of the reaction medium, even to above 10. This creates favorable conditions for the dissociation of H_2S, and then for its oxidation. The reaction sequence when calcium oxide is applied is shown in paper [22].

Examples of commercially available activated carbons are: Midas OCM from the company US Filters, manufactured from bituminous coal; Draco H_2S from the company Norit and S-208C from the company Waterlink/Barnabey Sutcliffe [22, 36]. For the removal of H_2S from the biogas, activated carbons from the company Gryfskand can also be used under technical names: AKPA-22, AKP-5, NG I, NG II, AG and AG-5S [40] and KOH-modified carbones from Desotec Polska, designed to remove acid gases with symbols: Airpel 10-3 and Airpel 10-4 [39].

Molecular sieves and synthetic silicas can also be used for desulphurization of biogas [22, 41, 42]. The molecular sieve grains have a spherical shape, with pores of similar dimensions, and their specific surface area is usually between 500 and 1000 m^2/g. Sorption of hydrogen sulphide with sieves depends on pressure and temperature. The upper limit of their thermal resistance is in the range 880-1100 K. Molecular sieves produced from polymorphic silicon can adsorb small organic molecules, but do not adsorb the polar water molecules. Water vapor can be adsorbed successfully with natural or synthetic zeolites - metal hydrates: Ca, Na, Mg or a combination thereof. Hydrogen sulfide can be adsorbed with a pore diameter of 0.4 nm [44].

Removal of hydrogen sulphide from biogas using haloisite sorbent

Haloisite is a double-layered aluminosilicate with a high specific surface area (65-400 m^2/g). It has the ability to absorb gases and liquids, is chemically and thermally resistant. The only mine of this material in Europe is the mine "Dunino" in Gliwice. This material can be used in biogas hydrogen sulphide removal filters as presented in the 2012 Baltic Biogas Forum [24]. Filters with three layers of haloisite sorbent are very effective in the purification process of biogas from hydrogen sulfide, siloxanes, ammonia, mercaptans, heavy metals (especially mercury). As a result of the mixing of haloisite with organic matter and providing conditions for the development of proper bacterial cultures, haloisite biodeposits are formed. Some of the biogas impurities are removed by bacteria and the rest is absorbed by the mineral sorbent. The advantage of these filters compared to natural biofilters (based on bark, roots, etc.) is that they retain their spatial structure and mechanical strength for a long time. In turn, this improves the efficiency of the purification process, facilitates the implementation of the entire process, and lowers operating costs [24, 45].

Removal of hydrogen sulphide using iron (III) and MgO ions deposited on a ceramic catalyst

A ceramic foam bed containing Fe^{3+} ions, in a heterogeneous catalytic system reversibly reduced to Fe^{2+}, enables the decomposition of hydrogen sulphide. The following reaction equations illustrate the mechanism of oxidation of hydrogen sulphide by Fe^{3+} ions and their regeneration using oxygen from the air [46].

$$H_2S_{(g)} \rightarrow S^{2-} + 2H^+$$

$$2Fe^{3+} + S^{2-} \rightarrow S^o + 2Fe^{2+}$$

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O$$

General reaction:

$$2H_2S + O_2 \rightarrow 2S + 2H_2O$$

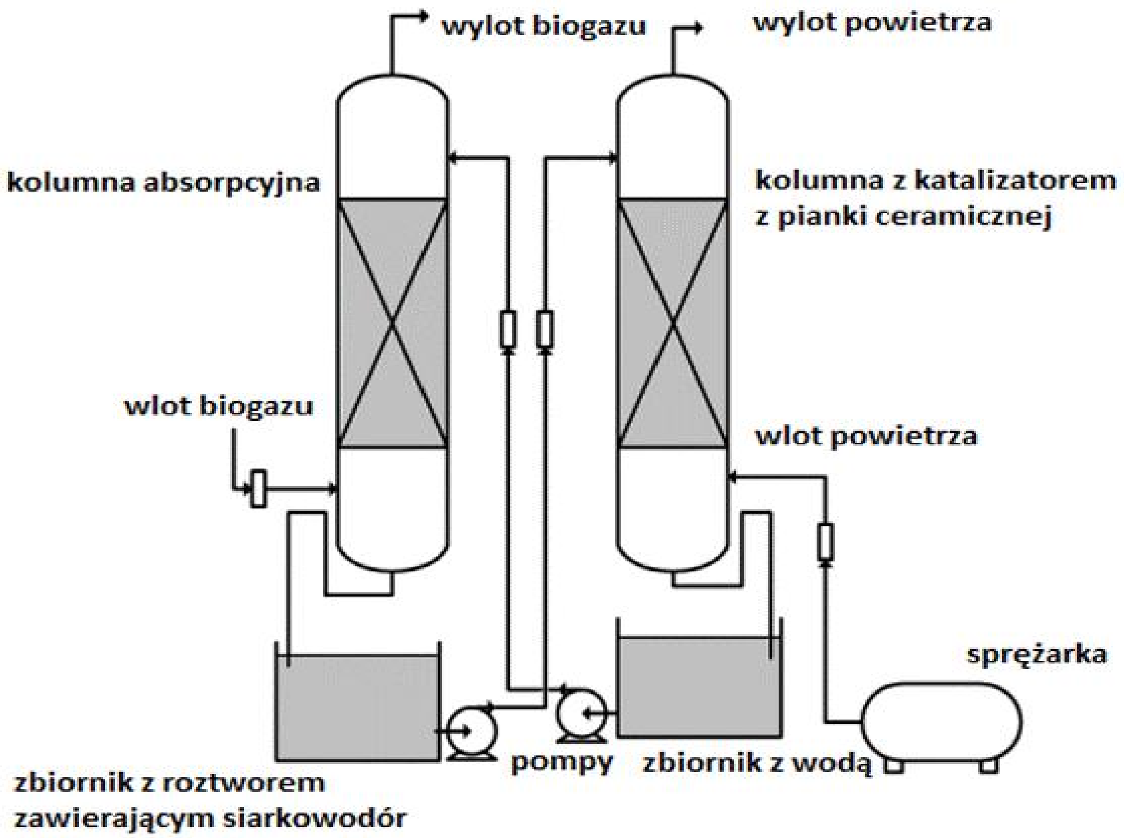

Fig. 2. Scheme of installation for the removal of hydrogen sulphide from biogas [47]

Source: N. Rakmak, W. Wiyaratn, J. Chungsiriporn, Removal of H_2S from biogas by iron (Fe^{3+}) doped MgO on ceramic honey-comb catalyst using double packed columns system. Engineering Journal, (1)14 (2010), 15-24.

The installation for the removal of hydrogen sulphide from biogas consisting of absorption column and catalytic column is shown in Figure 2. Biogas contaminated with hydrogen sulphide in the concentration range from 1300 to 1500 ppm was continuously fed to the lower part of the absorption column filled with Rashig rings. The column was sprayed with deionized water and the outlet of the purified biogas was on top. The H_2S containing solution was then pumped into the catalytic oxidation column of hydrogen sulphide. This column was filled with a monolithic catalytic oxidation bed that absorbed hydrogen sulphide in water. As a catalyst, Fe^{3+} with MgO admixture embedded on a ceramic foam was used. The catalyst bed was regenerated by oxygen from the air stream. The samples of biogas to be analyzed were taken at the inlet and outlet of the medium [46, 47].

Regeneration and unit capacity of solid sorbents

Table 2 contains data on methods of regeneration of solid sorbents and their sorption capacities, not included in the above section of the paper.

Table 1. Methods of regeneration of selected solid sorbents and their sorption capacity [20]

Sorbent	Method of regeneration of solid sorbent	Sorption capacity (hereinafter called H_2S sorption) in gH_2S/kg of sorbent	Literature position
Modified sodden ore (Strzyżów)	By exposure to the controlled interaction of oxygen from atmospheric air.	Sorption capacity **72 g(H_2S)/kg of dry mass**	[32, 48]
Bauxite sludge	Regeneration through the interaction of atmospheric air onto the bed. However, this process is not recommended	Sorption capacity in the range of 5.45-12.57 g(H_2S)/kg of dry mass of bauxite sludge.	[31]

	because the fresh sludge is characterized by a significantly higher efficiency of the H_2S sorption process than the regenerated sludge.		
Active carbon not modified	Regeneration usually at elevated temperature, water vapor or air.	Average sorption capacity 20 g(H_2S)/kg of carbon.*	[22, 34]
		Sorption of 1.67 gH_2S/kg of commercial carbon from nut shells was determined at T=30°C and 1.41 gH_2S/kg of carbon at T=550°C.*	[49]
		Sorption 7.1 gH_2S/kg of coal.	[31]
Modified active carbon	Regeneration usually at elevated temperature, water vapor or air.	Sorption on four carbons of hydrous biogas was in the range 36-608 gH_2S/kg of coal.*	[22, 36]
		Sorption on four carbons of dry biogas was in the range 9-106 gH_2S/kg of coal.* Sorption on four moist carbons of biogas was in the range 24-152 gH_2S/kg of coal.*	[22, 50]
		Sorption in the range of 20-110 gH_2S/kg of carbon at T=30°C depending on other parameters of the experiment.*	[33]
		Sorption in the range of 4.45-40.02 gH_2S/kg of carbon at T=550°C depending on the type of impregnating agent.	[49]
		Sorption through the ion-modified carbon OH^- was at an average level of 150 gH_2S/kg of coal.	[34]
Molecular sieve type NaX	Reduced pressure (0.005 mbar), temperature 75°C.	Sorption amounted to 80 gH_2S/kg of the sieve at 25°C, at a pressure of about 6.7 kPa.	[22]
Silica (synthetic silica TRI-PE-MCM-41)	Reduced pressure (0.005 mbar), temperature 75°C.	Sorption 5.9 gH_2S/kg of sorbent.	[31]
		The sorption capacity of pure hydrogen sulphide is about 100 g H_2S/kg of silica at T=25°C and p=1 atm.	[22, 42]
Halogenated Sorbent (PTH Intermark, Gliwice)	Autoregeneration with oxygen from the air - controlled flow, because excess air in the initial phase of regeneration can cause sulphur ignition in the haloisite deposit.	Sorption capacity about 300 gH_2S/kg of sorbent.	Data provided by Professor Jan Cebula, ATH in Bielsko Biała.

*The absorption of hydrogen sulphide depends on the temperature, presence of water vapor, type of sorbent and its physicochemical characteristics. Therefore, the values given in the paper are only approximate.

Source: Own summary based on a review of literature

Conclusion

The increase in biogas production and the new possibilities of its use force the improvement of methods of hydrogen sulphide removal. Currently in many biogas plants both in Poland and abroad, hydrogen sulphide is removed from biogas by adsorption on solid sorbents, usually containing iron (III) oxides, especially in the form of natural or modified sodden ore, as well as on activated carbons. These are usually simple, cheap, and relatively effective technologies worthy of universal use.

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