Effects of temperature, pH and O_2 on the removal of hydrogen sulfide from biogas by external biological desulfurization in a full scale fixed-bed trickling bioreactor (FBTB)

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Abstract: Hydrogen sulfide (H_2S) is a critical component of biogas formed under anaerobic conditions by sulfur and sulfate reducing bacteria from animal manure and renewable energy crops. H_2S causes high corrosion in equipment, has a negative environmental impact, inhibits the biogas formation process and is furthermore odorous and toxic. Although several methods for internal and external desulfurization found their way into practice and had been explored at laboratory scale, no data were available on the performance of such methods in full scale practice, especially for an external fixed-bed trickling bioreactor (FBTB). The effects of temperature, pH and air ratio on H_2S removal efficiency (RE) were studied. The study was conducted at a research biogas plant with a given output of 96 m^3 biogas per hour, and an H_2S concentration ranging between 500 ppm and 600 ppm (1 ppm=1 cm^3/m^3) on average. The FBTB column has been designed to hold a packing volume of 2.21 m^3 at a gas retention time of 84 seconds being loaded at an average of 32.88 g $H_2S/(m^3 \cdot h)$. The highest H_2S RE of 98% was found at temperatures between 30℃ and 40℃. A major decline in RE to 21%-45% was observed at temperatures from 5℃ to 25℃. The results clearly showed a temperature optimum range for sulfate reducing bacteria. The results reveal that RE is little affected by different pH values and air ratios. During the experimental period, the practical suitability of the FBTB system could be proved while avoiding the disadvantages of internal biological desulfurization methods.

Keywords: external biological desulfurization, fixed-bed trickling bioreactor (FBTB), H_2S removal efficiency (RE), hydrogen sulfide, biogas, full scale biogas research plant

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1 Introduction

In the course of the objective target of the European Parliament and the Council of the European Union to cover 20% of the total energy production in Europe with renewable sources by 2020[1], the use of renewable energy has increased during recent years. In this context the use of biomass has been increased significantly throughout Europe till now, supplying more than 69% of all renewable energy, followed by hydropower (19%),

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wind power (7%) and others (5%)[2]. In Germany, renewable energy sources contribute to 12.2% of the final energy consumption, with a share of 38% generated by wind power plants, 30% by biomass, 16% by hydropower and approximately 16% by photovoltaic power plants[3]. Especially in Germany, the production of biogas, which is produced by microbial anaerobic conversion, has an increasing importance for the supply of electric power. In 2012, the number of biogas plants in Germany with on-site electricity production was estimated to be 7 521 with a total capacity of 3 185 MW of electric power[4]. Based on the assumption that 83 new biogas upgrading plants are in use since 2012, supplying the grid with 460 million Nm^3 biomethane (~220 MWel. or 0.6% of the German natural gas consumption), almost 98.9% of all biogas plants use Combined Heat and Power (CHP) Units for energy production[5]. The renewable energy source “biogas” is defined as mixture of gases, consisting of methane (CH_4), carbon dioxide (CO_2), hydrogen sulfide (H_2S) and traces of other gases like nitrogen (N_2), oxygen (O_2), hydrogen (H_2) and ammonia (NH_3). The composition of biogas depends on the organic material as well as on the conversion technology used, varying between 50%-75% CH_4, 25%-45% CO_2 and 0-20 000 ppm (1 ppm=1 cm^3/m^3) H_2S[6,7]. The concentration of the especially significant trace gas H_2S in biogas is influenced by the composition of the organic material fermented[8]. Table 1 illustrates the sulfur (S) content of typical biogas substrates in percent of fresh matter[9]. The range of H_2S varies from 10 ppm to about 10 000 ppm[8]. H_2S is created through anaerobic fermentation of sulfate-containing feedstock, such as rapeseed or animal excrements[10]. It is created through microbial reduction of inorganic sulfate by sulfate reducing bacteria in the digester[11]. Academic literature, however, still lacks in reliable data on detailed conversion rates of inorganic sulfate to H_2S for typical biogas substrates. Sulfur deficiency in crop production is described to be a major problem in most parts of the world, due to higher crop yields, decreasing aerial deposition of sulfur and decreasing mineralization of S from soil organic matter[12]. The recovery of sulfur from the biogas process can help to compensate this shortage. Grant[12] reported that sulfate forms of S in fertilizers are immediately plant-available and good sources for use in the year of application, whereas elemental sulfur must oxidize to sulfate. However, this may require a certain process depending on environmental conditions, before it is plant-available in the year of application.

Table 1 Sulfur content in % of fresh matter and in g/kg for typical biogas substrates

Substrate	Sulfur content in % fresh matter
Maize silage	0.05-0.07
Grassland	0.05-0.08
Winter oilseed rape	0.061-1.14

Substrate	Sulfur content in g/kg
Cattle manure	0.7-0.8
Poultry manure	2.8-3.2
Cattle slurry	4.0-6.0
Pig slurry	6.0-7.0

H_2S, a kind of highly toxic[13,14] and corrosive gas[15], inhibits the biogas process directly, as well as indirectly in the case of higher H_2S concentrations in the fermenter[10]. The reduction of substrate-bound elementary sulfur and sulfates to H_2S is a competing reaction to hydrogenotrophic methane formation[10]. More importantly, the corrosive aspect is one of the main challenges, resulting in an acidification of the CHP-engine oil, deposits, adhesive contacts and harmful gas emissions during combustion[15]. The destruction of oxidation catalysts leads to increased operating costs (e.g., shorter oil change intervals) and reduced sales through engine failures. It finally results in a shorter lifetime of the CHPs and its components.

To avoid those negative impacts, a reduction of the H_2S-concentration in biogas is required before combustion. Internal and external desulfurization methods are well known and employed in most biogas plant using CHP units[16]. Chemical oxidation, carbon adsorption and external biological desulfurization are among the most commonly used methods for external desulfurization[17].

Biological desulfurization via injection of ambient air into the gas headspace in the digester is the most widely used process for internal desulfurization applied in 90% of all biogas plants and followed by the addition of iron salts to the fermenting substrate[18]. Depending on the proportion of oxygen injected into the gas phase, H_2S is oxidized into elementary sulfur, sulfate-S or sulfite-S[19]. A reformation of S into H_2S by an unintended return of accumulated degradation products from the colonization surfaces into the fermentation substrate is one of the crucial drawbacks of this method[20].

Recently, external biological desulfurization methods have become much more popular in order to remediate the problems resulting from internal desulfurization. Biogas plants with external desulfurization units are finding their way into the market. Several methods for external biological desulfurization such as two-stage bioscrubbers, one stage-biotrickling filter have been described in the literature[21,22]. In two-stage bioscrubbers, the H_2S in the raw gas is absorbed first by contacting with water in a scrubber and afterwards biologically degraded in a bioreactor[23]. A further option is a one-stage bio-trickling filter, where the raw biogas passes through a fixed bed reactor, filled with plastic packing materials. Washing water is trickled periodically over the fixed bed to promote a biofilm generation on the packing material, enabling the immobilization of microorganisms. Dissolved H_2S is oxidized by certain microbial group to elementary sulfur and sulfate[24]. The H_2S degradation rate of the bacteria depends on several parameters which could be better controlled with a recirculated water phase (pH, temperature, addition of nutrients, removal of accumulated salts, etc.)[25]. The effects of different operational settings for pH, oxygen and temperature have been described in recent literature. Especially, a wide range of pH was reported for H_2S removal in biofilters. Gabriel and Deshuesses[26] have discovered that pH levels decreased during the adaptation phase and stabilized at pH 2. The decrease in pH resulted in an increased hydrogen sulfide degradation rate up to 99%[26]. Another study showed pH values ranging from 2 to 7 and observed removal efficiencies from about 95% at pH 2, to 97% at pH values from 3 to 7[27]. Other experiments in the mentioned study revealed an optimal pH value of 6 for autotrophic bacteria. These differences in degradation performance for different pH values are explained by the fact that within the genus of the sulfur compound bacteria *Thiobacillus*, some species are found favoring pH-neutral environments and others favoring low pH values[25]. An insufficient availability of oxygen in the bioreactor leads to an incomplete removal of H_2S[28]. Schneider et al.[29] reported a stochiometric demand of 4%-6% (v/v) air in biogas as optimal for a complete oxidation. For the degradation of organic compounds they recommended a higher air flow rate to provide the microorganisms with sufficient oxygen. For an optimal desulfurization performance, an amount of about 8%-12% air fed into the biogas flow was suggested by Mollekopf et al[19]. It was reported that higher air application rates resulted in lower CH_4 content in the biogas and a lower calorific value[19]. The influence of temperature on H_2S degradation was studied by Schneider et al.[29] and revealed an impairment of microorganism activity, which led to a reduction of the degradation capacity at temperatures below 20℃ in a bio-scrubber. For maximum H_2S degradation, the study of Mollekopf et al.[19] revealed an optimal washing water temperature at 35℃, due to an increased bacterial activity at higher temperatures. Furthermore, the study showed that temperatures above 35℃ inhibit the microbial activity and reduce the degradation of H_2S[19].

The present scientific work intends to test the efficiency of a full scale external biological desulfurization plant. The fixed-bed trickling bioreactor (FBTB) was integrated on the research biogas plant, at the experimental station Unterer Lindenhof (University of Hohenheim). For this purpose, a FBTB was investigated in order to determine the effect of each operational parameter such as pH, O_2 content and temperature degradation products on FBTB performance under full-scale conditions. To the best of our knowledge, this is the first literature to report on the performance of a full-scale FBTB for H_2S biogas treatment.

2 Materials and methods

2.1 Experimental setup

The FBTB “BioSulfidEx” was investigated on the research biogas plant “Unterer Lindenhof”, an experimental station of the University of Hohenheim. The biogas plant consists of two digesters (each with a volume of 923 m^3) with concrete coating and one secondary digester (volume 923 m^3), fitted with a double membrane roof for gas storage. The gas is combusted inside a gas-otto-engine with a capacity of 186 kW$_{el}$ and 202 kW$_{th}$ power. Depending on the respective availability, approximately eight tonnes of liquid and solid manure from cow, pig, sheep or poultry husbandry are required for the daily biogas production in both digesters, with addition of approximately eight tonnes of renewable energy crops such as maize silage, grass silage, whole crop silage and ground grain. The organic loading rate related to the organic dry matter (Br$_{ODM}$) equals 1.93 kg/m^3·d with a hydraulic retention time (HRT) of 120 days in total[30]. Under mesophilic conditions, around 96 m^3/h of biogas is produced, at a quality of approximately 52% CH_4, 48% CO_2 and 500 ppm to 600 ppm H_2S. The raw biogas formed in both digesters is stored in the secondary digester, later on supplying the Combined Heat and Power Unit. With the installment of the FBTB, the regular desulfurization method was replaced, originally consisting of biological desulfurization by 0.5% air injection into all three digesters and including a final biogas cleaning, before entering the CHP unit by an activated carbon filter (used as a polishing filter). The desulfurization unit (DSU) was integrated into the gas pipeline, between the secondary digester and the CHP-unit. The FBTB column has been designed to hold a packing volume of 2.21 m^3 at a gas retention time of 84 seconds being loaded at an average of 32.88 g H_2S/m^3·h.

The DSU consists of one FBTB and a subsequent carbon filter thereby a complete desulfurization is ensured in case of a FBTB breakdown. At regular conditions, the gas flows from the secondary digester into the FBTB and then through the activated carbon filter (both in upstream mode), before entering the CHP-unit. Various operation modes can be chosen by adjusting different gate valves to run either the FBTB or the carbon filter independently. Alternatively, the DSU can be shut down (Figure 1). Ambient air is injected by three air compressors into the biogas supply pipeline in front of the FBTB, while volume flow is adjusted by ball valves. A flow monitor, controlling the biogas flow, turns the air-compressors on and off, in case of a CHP stop, hereby preventing a surplus of air entering the system and causing technical or safety problems (Figure 1).

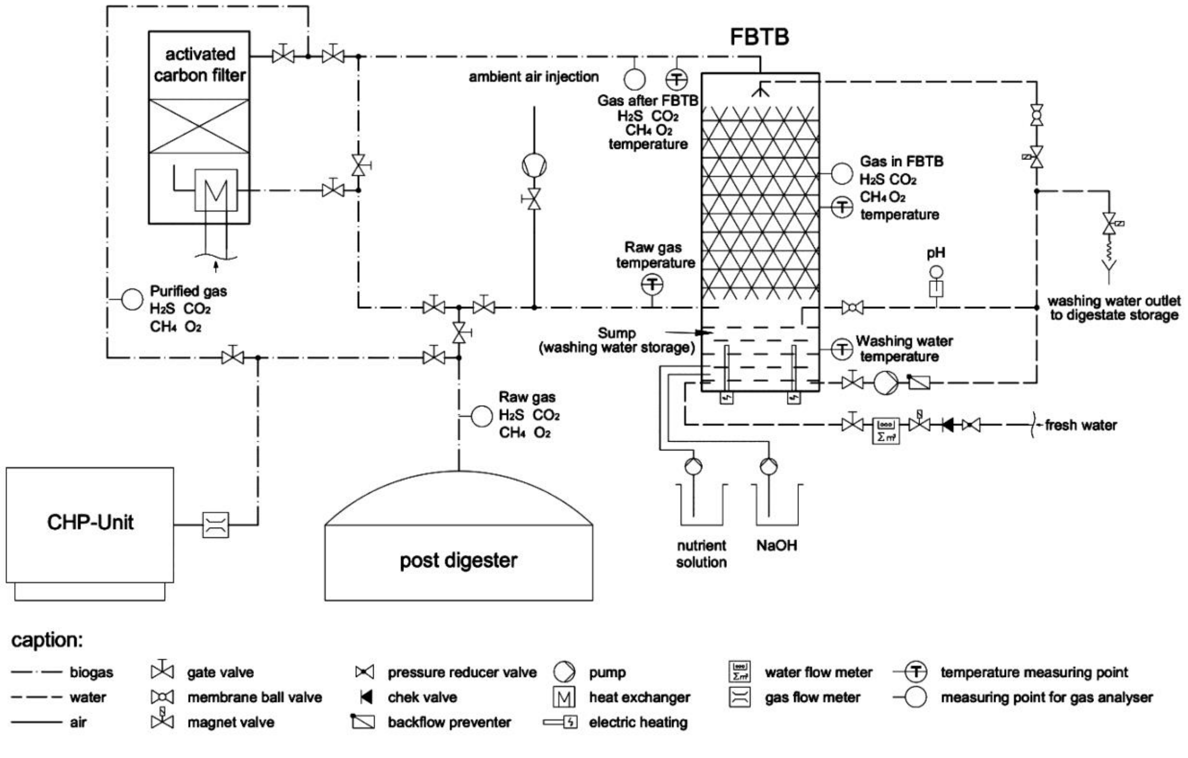


Figure 1 Piping diagram and instrumental drawing of the DSU

The non-insulated FBTB column is made up of polyethylene (PE) and filled with fixed-bed packing material for surface and bioreaction volume enlargement, with a volume of 2.21 m^3 above the gas supply pipe. The lower part of the FBTB (sump) is used for washing water storage, with a maximum capacity of 0.4 m^3. Four electric heating systems in the sump allow an adjustment of the washing water temperature, which is independent from the ambient temperature. The washing water in the sump was continuously circulated by a pump to allow permanent pH measurement. The fixed-bed was percolated with washing water from the sump for two minutes with ten-minute intervals and exchanged with fresh water every 1.5 hours for four minutes. The washing water containing decomposition products is flushed out before the fresh water is supplied. A membrane pump injects a small dosage of screened manure (as nutrient solution: 4 410 mg/L N, 250 mg/ L P, 4 860 mg/ L K) into the sump, while fresh water is added. To maintain the pH-value in the washing water, NaOH is injected into the sump by a membrane pump (controlled by a pH-measuring transducer). The insulated carbon filter was heated by a water heat exchanger, in order to reduce condensate formation (Figure 1).

2.2 Measurement equipment

As shown in Table 2, numerous measuring devices were installed at the biogas plant. This was to ensure the accurate measurement of all operating and consumption data. Gas quality was analyzed in a cycle of approximate 3.3 h by a multisensor analyzing system Union INCA 4000 (Union Instruments GmbH, Germany) for CH_4, CO_2, H_2S and O_2 at four different measuring points: raw gas; gas in FBTB; gas after FBTB and purified gas. CH_4 (measurement range and accuracy 0-100% Vol. ±1%) and CO_2 (0-100% Vol. ±1%) were measured by a nondispersive infrared (NDIR) sensor, H_2S (0-5 000 ppm ±5% & 5 000-10 000 ppm ±10%) and O_2 (0-25% Vol. ±1%) with electrochemical sensors. The gas quantity was continuously measured before the CHP unit by Esters (Esters Elektronic GmbH, Germany) GD 100/50/3 Ex gas flow meter based on the Fluidistor measurement principle. Temperatures were detected every 15 minutes by NiCr-Ni temperature gauges GTF 103 G ½ (Greisinger Elektronik GmbH, Germany) at four measurement points: raw gas, gas in FBTB, gas after FBTB and washing water temperature. The measurements were stored in Testo (Testo AG, Germany) 175-T3 data loggers. The ambient temperature was logged with two Testo Type 175-H2 data loggers. The pH-value was measured by a universal glass electrode line 201020 (JUMO GmbH & Co. KG, Germany) in the washing water pipeline after the circulation pump. The pH-electrode was thereby calibrated trough a two-point calibration, every second week. The data of gas quality and quantity were stored automatically at the central control system of the biogas plant and the pH-value data was saved by the central control system of the DSU. Electrical energy and water consumption were also captured by an active current counter Finder 7E (FINDER S.p.A., Italy) and a water flow Meter (N/A) (Table 2).

Table 2 Measuring instruments, measuring point and measuring interval

Measurement	Unit	Measuring point	Measuring interval
Gas analyzer Union INCA 4000			
CH_4	%	Raw gas; gas in FBTB; gas after FBTB; purified gas	20 min, every 3.3 h
CO_2	%	Raw gas; gas in FBTB; gas after FBTB; purified gas	20 min, every 3.3 h
O_2	%	Raw gas; gas in FBTB; gas after FBTB; purified gas	20 min, every 3.3 h
H_2S	ppm	Raw gas; gas in FBTB; gas after FBTB; purified gas	20 min, every 3.3 h
Esters GD 100/50/3 Ex			
Gas quantity	m^3/h	Gas supply pipe CHP-Unit	Continuously
Jumo 202535			
pH-value		Washing water after circulation pump	Every 10 min
Temperature sensor GTF 103, data logger 175-T3			
Temperature	℃	Raw gas; gas in FBTB; gas after FBTB; washing water	Every 15 min
Water flow meter			
Water consumption	m^3	Water inlet	Continuously
Finder 7E.36.8.400.0000			
Active current counter	kWh	Power inlet	Continuously

2.3 Laboratory analysis

The washing water was analyzed for the degradation products such as total sulfur, sulfate and sulfite every week at an external laboratory (Synlab Stuttgart). The sulfate and sulfite content was determined by ion chromatography (IC) and total sulfur by inductively coupled plasma mass spectrometry (ICP-MS) (Table 3).

Table 3 Laboratory analysis plan and method

Measurement	Unit	Measuring method	Measuring interval
Total sulfur	mg/L	DIN EN ISO 11885 (E22)	Once per week
Sulfate	mg/L	DIN EN ISO 10304-2	Once per week
Sulfite	mg/L	DIN EN ISO 10304-3 (D22)	Once per week

2.4 Experimental phases

The experiments were split into six different experimental periods (EP), as shown in Table 4. Following a trial run, the desulfurization bacteria in the first EP were expected to grow and adapt themselves to the fixed-bed material and to the conditions of the DSU. The oxygen content was kept at 1%. No external pH-regulation was used, thus the pH level adjusted itself, depending on the rising acidification capacity through H_2S degradation. The washing water temperature was not regulated initially, but influenced by the raw gas and ambient temperature. As it is reported in literature, temperature is a key factor for high H_2S elimination capacities, therefore the effect of FBTB heating was investigated during EP 2. In the following four experimental periods, the influence of washing water pH (pH 2 and pH 7, respectively) and oxygen content of 0.5% and 2% in the biogas on the H_2S-elimination capacity was analyzed. The heating system was not used during summer time, hereby addressing EP 3 and 4. An electrical heating system was used for EP 5 and 6 during autumn and winter, to keep the washing water temperature at a level of approximately 35℃. Hereby, the negative effect of fluctuating ambient temperatures could be minimized.

Table 4 Experimental plan

Phase	Experimental days	pH-value	O_2-content	Washing water temperature
Experimental period 1 (adaptation phase)	52	No control	1%	Variable
Experimental period 2 (temperature influence)	60	2	0.5%	10 - ~ 35℃
Experimental period 3	26	7	0.5%	Variable
Experimental period 4	30	7	2%	Variable
Experimental period 5	22	2	2%	~ 35℃
Experimental period 6	28	2	0.5%	~ 35℃

2.5 Analyses

H_2S-loading is calculated as a function of inlet gas flow and H_2S concentration over the filter volume in relation to molecular mass of H_2S and the molecular standard volume of gases as shown in Equation (1).

$$\text{Loading}=\frac{\text{gas flow }\left[\frac{\text{l}}{\text{h}}\right]\ \text{H}_2\text{S}_{\text{input}}\ [\text{ppm}]\ \ 34.08\ \left[\frac{\text{g}}{\text{mol}}\right]}{\text{filter volume }[\text{m}^3]\ \ 22.41\ \left[\frac{\text{l}}{\text{mol}}\right]\ 10^6} \tag{1}$$

The removal efficiency (RE) of H_2S in the FBTB is calculated as given in Equation (2).

$$\text{Removal efficiency} = \frac{(\text{H}_2\ \text{S}_{\text{Input}}\ [\text{ppm}] - \text{H}_2\ \text{S}_{\text{Output}}\ [\text{ppm}]}{\text{H}_2\ \text{S}_{\text{Input}}\ [\text{ppm}]} \times 100\% \tag{2}$$

The elimination capacity (EC) of the FBTB is given by the H_2S-input concentration minus H_2S-output concentration multiplied with the gas-flow and divided by the filter volume, as shown in Equation (3).

$$\text{EC}=\frac{\text{gas flow }\left[\frac{\text{l}}{\text{h}}\right]\left(\text{H}_2\text{S}_{\text{input}}\ [\text{ppm}] - \text{H}_2\text{S}_{\text{output}}\ [\text{ppm}]\right)\ 34.08\ [\frac{\text{g}}{\text{mol}}]}{\text{filter volume }[\text{m}^3]\ \ 22.41\ [\frac{\text{l}}{\text{mol}}]\ 10^6} \tag{3}$$

To compare the sulfate, sulfite and total sulfur content in the washing water, the data had been converted from sulfate into sulfate-S, from sulfite into sulfite-S and from total sulfur into elementary sulphur, by multiplying with a conversion factor that reduces the influence of oxygen weight (Equations (4), (5), and (6)).

$$\text{Sulfate-S [mg/L]} = \text{Sulfate [mg/L]} \cdot \frac{1}{2} \tag{4}$$

$$\text{Sulfite-S [mg/L]} = \text{Sulfite [mg/L]} \cdot \frac{2}{3} \tag{5}$$

$$\begin{aligned} \text{S}_{\text{elementary}}\ \text{[mg/L]} &= \text{Total sulfur [mg/L]} - \\ &\text{Sulfate-S [mg/L]} - \text{Sulfite-S [mg/L]} \end{aligned} \tag{6}$$

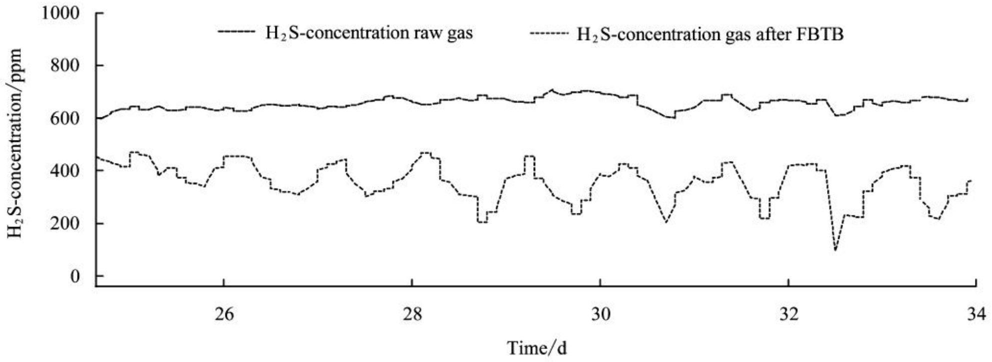
The data of the experimental periods 2-6 were divided into groups and statistically evaluated.

3 Results

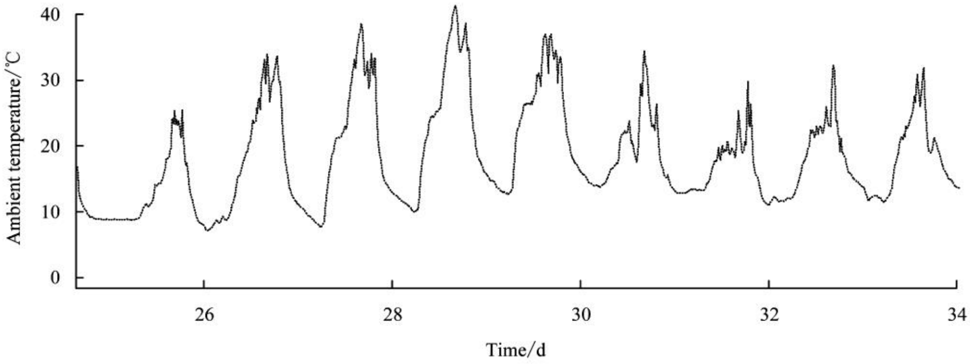
3.1 Adaption phase-EP 1

Figure 2 shows the ambient air temperatures, H_2S concentrations and RE during the adaption phase.

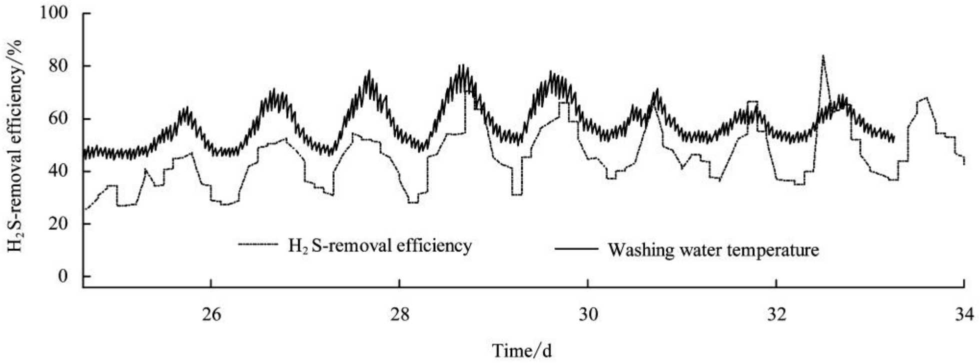
In Figure 2a, the time is plotted over the H_2S-concentration in the raw gas and after the FBTB during the adaption period. The y-axis represents the H_2S-concentration in ppm, while the x-axis stands for the time in days. Figure 2b shows the ambient temperature over the time line of the adaption phase and finally Figure 2c shows the H_2S-removal efficiency and the washing water temperature.



a. H_2S-concentrations in the raw gas and in the gas after FBTB



b. The ambient temperature



c. The removal efficiency and the washing water temperature during EP 1 "adaption phase"

Figure 2 Air temperatures, H_2S concentrations and removal efficiency during the adaption phase

Over the adaption period, the H_2S-concentration of the raw biogas ranged between 600 and 800 ppm, while the H_2S-concentration after the FBTB fluctuated within a wide range. It could only be lowered down to a minimum of 200 ppm, but could not be kept at a constant level. After day 24, the margin between the raw gas and gas after the FBTB expanded. High variations in H_2S-concentrations after the FBTB could be observed.

Fluctuations closely linked to temperature were obviously caused by the alternation of day and night. At the same time, the ambient temperature values ranged between 5℃ and 40℃, with higher temperatures towards the end of the adaption phase. Over this monitored period, a variation of the H_2S RE and washing water temperature was detected. At washing water temperatures between 15℃ and 40℃, the H_2S RE fluctuated between 20% and 80%. It is quite obvious that the ambient temperature has a direct influence on the H_2S RE. Higher temperatures resulted in a better H_2S RE. In summary, a significant influence of the ambient temperature on the H_2S concentration in gas after FBTB was found. The higher the ambient temperature, the lower the H_2S-concentration after the FBTB was found. Day and night fluctuations are clearly visible (Figure 2).

3.2 Influence of temperature on the removal efficiency-EP2

The influence of temperature on the RE was investigated in the experimental period 2. The ambient temperature was fluctuating between -10℃ and 30℃, with an average value by approximately 8℃ during this period. The temperature of the washing water was kept at a range between 25℃ and 38℃ via a heating system. It was observed that the washing water temperature could vary between -5℃ and 25℃ when the heating system was turned off. The washing water temperature influenced the temperature in the FBTB significantly, while the RE changed rapidly with temperature fluctuations. Figure 3 shows the effect of temperature fluctuations on the RE. On the y-axis, the RE is plotted over eight temperature ranges from 0℃ to over 40℃.

The average RE was 21% at a temperature range of 0-10℃ and was then increased constantly to a level of ~ 45% at temperatures between 20 and 25℃. The variance of the RE varied within a wide range for each group of temperature range such as 0-10℃, 10-15℃ and 15-20℃. At an increase in temperature from 20-25℃ to 25-30℃, a sharp increase in the average RE (of up to ~ 90%) was monitored, hereby showing a decreasing variance. RE of up to 98% with very small variances were measured for the temperature ranges of 30-35℃ and 35-40℃. Above 40℃, a minor deterioration in RE (down to 95%) was observed with an increase in variance (Figure 3).

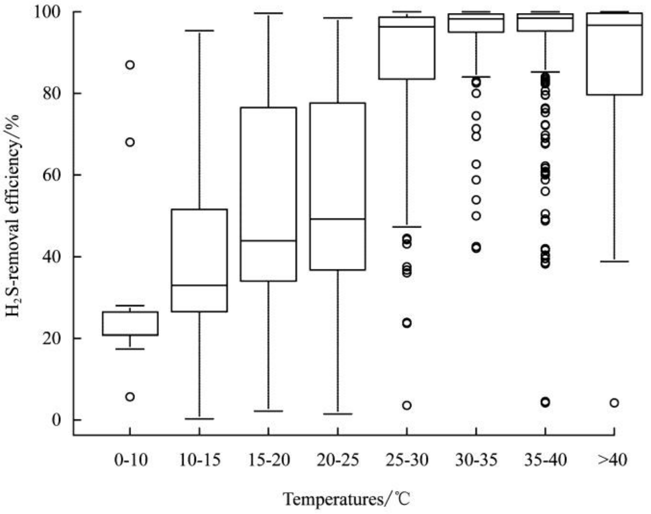
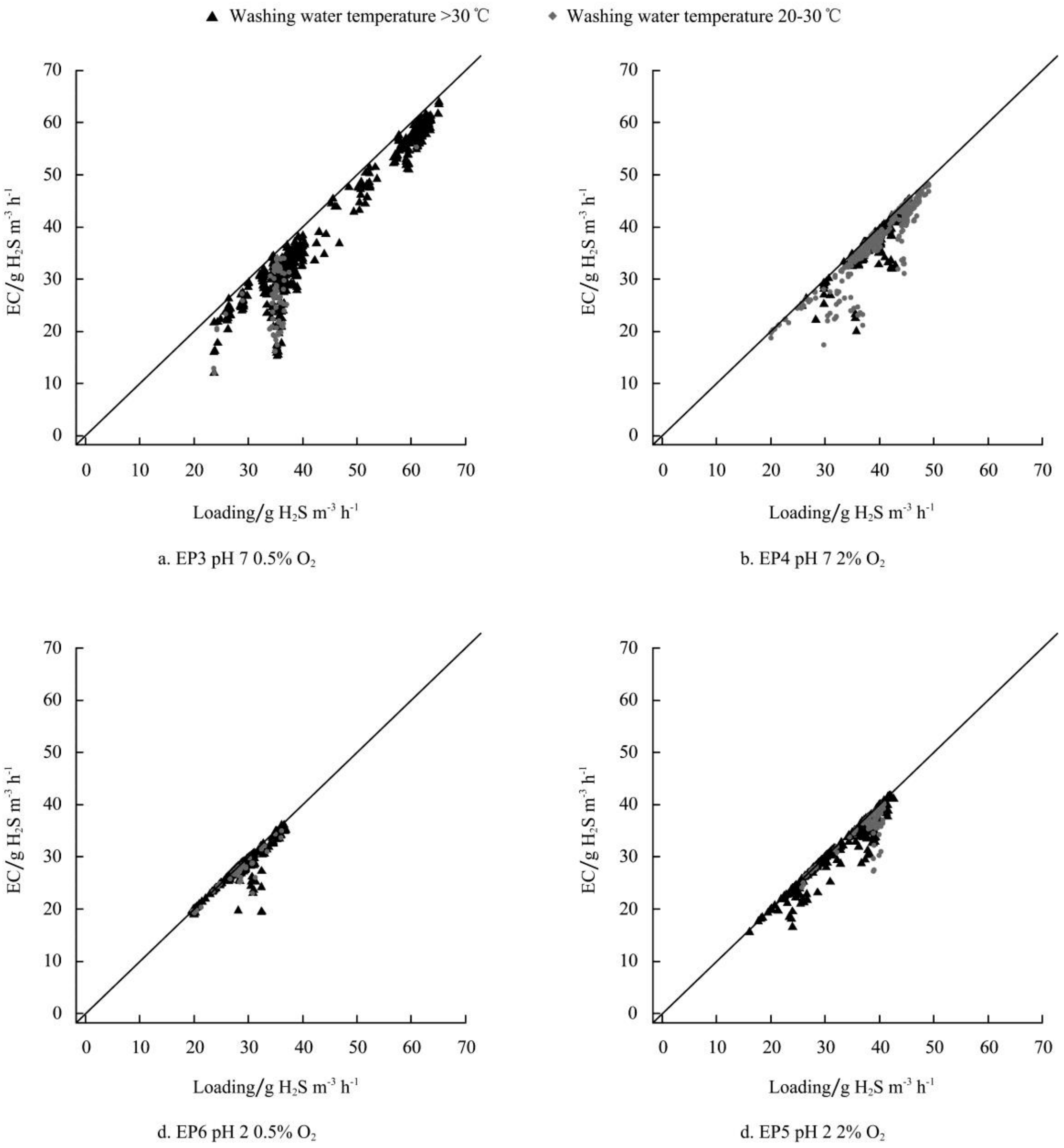


Figure 3 Influence of different washing water temperatures on the removal efficiency for experimental period 2

3.3 Influence of pH and O_2-content

In Figure 4, all results for the experimental periods (EP 3-6) are presented in one graph. The y-axis is given as elimination capacity (EC) in g H_2S m^{-3} h^{-1} over the H_2S loading in g H_2S m^{-3} h^{-1} on the x-axis (for the filter volume). The fitted line represents the 100% elimination capacity. For the sake of better understanding, this data has been divided into two classes: washing water temperatures between 20-30℃ and above 30℃. The closer the data comes to the line, the higher is the EC. At EP 3 and 4, at pH 7 and with O_2 at 0.5 and 2%, the FBTB remained unheated, but temperatures were kept above 20℃, influenced by warm summer climate conditions. During the transition period from autumn to winter, electric heating systems in the FBTB have been retrofitted to maintain a target temperature of approximately 35℃. The temperatures could be kept above 20℃ throughout the EP 3-6. A pH value of 7 was targeted in EP 3 and EP 4 and pH 2 was achieved in EP 5 and EP 6 by adding lye. In summary, no obvious influence of temperature levels on EC could be observed at temperatures above 20℃. The data depicted in EP 5 and 6, at constant heat supply, show a lower variance at high EC; with less data between 20-30℃, compared to

EP 3 and 4. At pH 7, a change from 0.5% (EP 3) to 2% (EP 4) of O_2 resulted in lower variance, whereas a change from 2% (EP 5) to 0.5% (EP 6) of O_2 at pH 2 showed no major deviation. At pH 2, a slightly increased EC was found. No definite correlation of pH and O_2 concentration on the EC was observed (Figure 4).



a. EP3 pH 7 0.5% O_2

b. EP4 pH 7 2% O_2

d. EP6 pH 2 0.5% O_2

d. EP5 pH 2 2% O_2

Figure 4 Link of loading in relation to the elimination capacity and the influence of temperature groups from 20-30℃ and over 30℃ described for the EP 3 (pH 7, 0.5% O_2), EP4 (pH 7, 2% O_2), EP5 (pH 2, 2% O_2) and EP6 (pH 2, 0.5% O_2)

Figure 5 shows the allocation of data for RE of the experimental periods 3-6. Again, this data comprises results for pH 7 and pH 2, at 0.5% and 2% oxygen supplies, with temperatures below and above 30℃.

On average, the RE was above 85% in all experimental periods. A higher RE was found for EP 5 and 6 at pH 2. An increase in RE can be observed at pH 7, when the oxygen supply increased from 0.5% to 2%. At pH 2 an inverse correlation could be observed. The highest RE was found in EP 6, with minor deviations in variance. At constant temperatures above 20℃, as it was measured for all experimental periods, a high RE could be achieved again, with less variance in summertime or at heat supply. No significant differences were found for temperature classes below and above 30℃. The results showed no clear causal link for pH and oxygen adaption on RE.

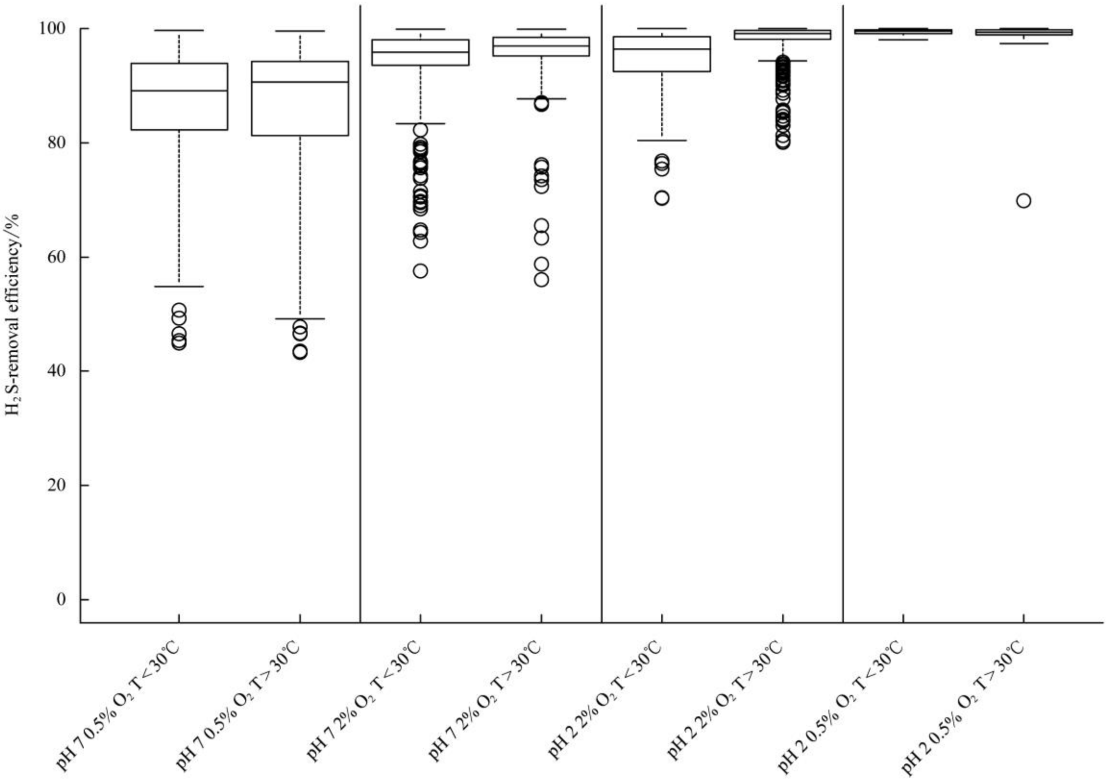


Figure 5 Boxplot depicts the influence of different temperature groups from 20-30℃ and over 30℃ at pH-values of 7 and 2 for O_2-content of 0.5%, and 2% on the removal efficiency for the experimental periods 3-6

3.4 Degradation products

In addition to the efficiency and the performance of the FBTB, the appearance and quantity of degradation products were of major interest in this study. The results of the samples analyzed at the laboratory are presented in Figure 6. They show the allocation of sulfate-S, sulfite-S and elementary sulfur in mg/L during the experimental periods 3-6. After H_2S was eliminated in the gas, the transformation products appeared in different concentrations in the washing water. As they are dissolved in the washing water, the degradation products are flushed out of the FBTB in defined periods. In EP 3, at pH 7 and 0.5% O_2, an amount of 334.89 mg/L of sulfate-S was found as the largest proportion, followed by elementary sulfur at 171.86 mg/L. An increase in sulfate-S to 580.83 mg/L and elementary sulfur to 431.54 mg/L was observed in EP 4 at pH 7 and 2% O_2. No elementary sulfur was found in EP 5 at pH 2 and 2% O_2 but 526.67 mg/L sulfate-S was determined. By lowering the oxygen supply to 0.5% at pH 2, the content of sulfate-S was found at 189 mg/L, with a minor amount of 20.6 mg/L elementary sulfur. Sulfite-S could only be determined in a significant quantity in EP 3. It was found, that at 2% oxygen supply the amount of sulfate-S was at its maximum. Elementary sulfur was found in measurable quantity and in a significant proportion at pH 7. To summarize the findings, it can be shown that the degradation products are found in the washing water and can therefore be flushed out of the FBTB system via a washing water outlet and reintroduced into the digestate

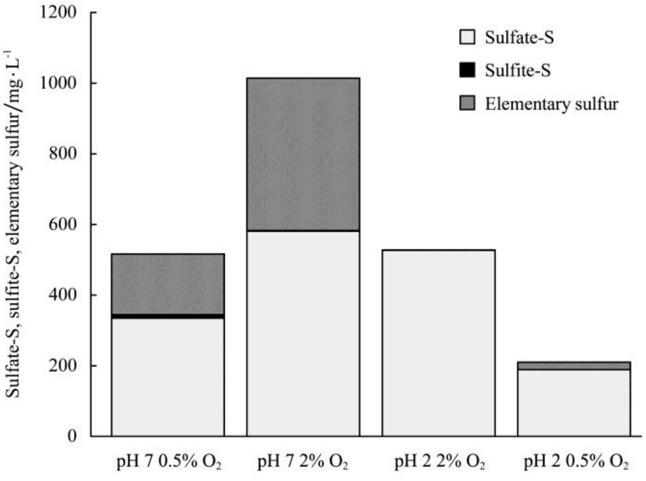


Figure 6 Composition of the degradation products sulfate-S, sulfite-S and elementary sulfur for the experimental periods 3-6

Storage, thus closing the nutrient cycle of the biogas plants. However, different sulfur components and quantities appeared, depending on the pH value and oxygen conditions (Figure 6).

3.5 Consumption of operating resources

Table 5 shows the consumption of operating resources in EP 1 and EP 3-6. The consumption of resources amounted to approximately 1 100 L/d water, ~25 kWh/d electric power and ~15 kWh/d of electric power for the washing water heating system. In EP 3 and 4, 4 L of lye and in EP 5 and 6, 0.6 L of lye were used per day to keep the pH-value at a constant level. To ensure the supply of nutrients in the washing water, ~2 L/d liquid and screened manure were dosed into the digester (Table 5).

Table 5 Consumption of operating resources for all experimental periods (EP)

	EP 1	EP 3	EP 4	EP 5	EP 6
	Adaption phase	pH 7 0.5% O_2	pH 7 2% O_2	pH 2 2% O_2	pH 2 0.5% O_2
Fresh water supply (L/d)	1103	1170	1188	966	10830
El. power consumption (kWh/d)	25.90	19.35	23.25	27.20	52.34
El. power heating (kWh/d)				10.2	21.45
Lye (L/d)		4	4	0.6	0.60
Liquid manure (L/d)	2.18	2.18	2.18	1.50	2.18

4 Discussion

The study of a FBTB under full-scale operational conditions appeared to have specific requirements and proved to be challenging. External influences and failures of measurement technique or technical breakdowns of the plant strongly affected the measurements. Keeping the settings for the different operating parameters at a constant level was one of the major challenges. A fluctuating ambient temperature had a decisive impact on temperatures in the FBTB, and on the washing water. Despite these challenges, reliable data of high quality could be gained and an excellent desulfurization performance could be achieved.

Throughout the experimental periods, the FBTB was able to provide a constant quality of purified biogas. The long duration of the adaption phase can be explained by starting of the plant in winter when temperatures were found below 0℃, thereby inhibiting bacterial growth. It was concluded that by adequate heat supply and insulation of the FBTB, the adaption phase can be shortened.

The results of EP 2 clearly confirm the significant influence of temperature in the FBTB and the washing water temperature on the RE, testifying best performance at a temperature range between 30℃ and 40℃. A direct influence of ambient temperature on temperature in the FBTB and on washing water could be observed. The living environment of the desulfurization bacteria responds immediately to low and high temperature in negative and positive way. The results proved that adequate heat supply, which can be achieved by heating the washing water or the biogas, is crucial for an efficient H_2S removal in the FBTB. In addition, an insulation of the FBTB can be strongly recommended. A replacement of the electrical heating system by a surplus heating system (supplied by CHP-unit) would be more energy efficient, due to the fact that heat oversupply is found at most biogas plants. The data for lower elimination capacities or removal efficiencies in Figures 2 and 3 could be explained by technical failures, e.g. pump or valve failure, thus leading to an absence of washing water trickled over the fixed bed. The improved elimination capacities in EP 5 and 6 could be the result of a stronger adaptation of the bacteria over time. The results of the temperature experiment are comparable to the results by Mollekopf et al.[19], who reported an optimum temperature of 35℃. Furthermore, the results of Schneider et al.[29] could be confirmed showing low efficiency of the FBTB at temperatures below 20℃ caused by the impairment of desulfurization bacteria.

No significant influence of different pH values could be noted. The results showed a slight increase in RE from pH 7 to pH 2. However, this could have superimposed by the effects of temperature fluctuations or technical failures. According to existing literature, various species of desulfurization bacteria are found, which have optimal living conditions at pH-values between pH 2 and pH 7[25]. These findings could be proved by the overall high desulfurization efficiencies found in this study. An important aspect of different pH values is the impact on consumption of operating resources and on corrosion behaviour. To keep the pH value at around 7, a large quantity of lye was needed to compensate the acidification, this causing an increased workload and rising variable costs. An enhanced corrosion exposure of the pump and all other metal parts was observed at a pH value of 2.

In the experimental periods with different oxygen concentrations, no clear effect on the H_2S RE was ascertained. At pH 7, an oxygen content of 2% was superior to 0.5% and was found at pH 2 being exactly the opposite[19]. In addition, the differences (as already discussed for the temperature influence), are too small to draw precise conclusions, as side effects could superimpose the results. Furthermore, no explicit influence of temperature could be observed at temperatures above 20℃. In contrast to the study by Schneider et al.[29], who recommended 4% to 6% vol. of air, a significantly lower amount of air (0.5% O_2 ~ 2.4% vol. air) was fed in this study. At 2% O_2 supply, the value of air reached 8% and 12% vol., as mentioned by Mollekopf et al.[19]. The effect of lower gas quality and an increasing gas quantity at high air application rates could be observed, leading to a dilution of methane as described by Mollekopf et al.[19]. The results of both studies could be confirmed, as high desulfurization efficiencies were found for both supply rates at 0.5% and 2% O_2. The experimental research has shown that at lower O_2 contents, the operation safety of the CHP-unit and the biogas plant safety improved. Based on the results of this study, the authors of this article can recommend 0.5% O_2 supply as adequate for desulfurization and optimal for general biogas plant safety.

The results of the laboratory analysis for degradation products vary heavily, although the samples were taken directly before the washing water was exchanged. A breakdown of elementary sulfur crusts, resulting in a formation of deposits on the column tray and, the influence of the sample taking, could be a possible explanation for the measured differences. These interferences could be reduced by an active mixing system in the column sump or by taking samples directly out of the column. As shown by Mollekopf et al.[19] a higher sulfate formation was observed at 2% oxygen supply. The results generally showed that the degradation products formed can be removed from the system by purging. The formation of strong sulfuric acid at pH 2 leads to a high corrosion on pumps and on all other metallic components. Therefore, a stringent material selection for all components is absolutely necessary. A clogging of pipes or the expansion material trough sulfur could not be determined during this study. Nevertheless, the sulfur deposits in the column sump should be removed after a preset time. To ensure an economic operation, the consumption of operating resources as well as the effort for technical maintenance should be kept at a constant low level. To obtain exact measurement data and operational safety, a high quality of measurement equipment and regular maintenance is required.

5 Conclusions

High removal efficiencies could be achieved under full-scale conditions with the FBTB investigated in this study. By using this method, external biological desulfurization confirmed the expected results and proved suitability for the given H_2S loadings. At the same time problems of internal biological desulfurization were avoided. A temperature of about 35℃ was shown to be absolutely inevitable for the efficiency of the process. Different oxygen contents did not have a significant effect on desulfurization efficiency, but 0.5% oxygen can be recommended for general plant safety. No direct conclusion can be drawn for the influence of the pH value as the desulfurization efficiency has been on a similar level. However, operation at pH 7 caused high consumption of operation resources, whereas pH 2 imposed particularly high requirements for anti-corrosion.

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