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Effect of Dosing PIX 113 Coagulant to the Batch on Mesophilic Fermentation Process and Reducing Hydrogen Sulfide Content in Biogas

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ABSTRACT

In certain concentrations, hydrogen sulfide – occurring in gaseous fuel – corrodes combustion chambers, contaminates and acidifies engine oil and has a destructive effect on engine seal components, valve seats and timing. Fuel in the form of digestate gas, before powering cogeneration units, must meet the standards set by the manufacturer of the unit. Whether such values can be achieved depends primarily on the concentration of hydrogen sulfide and the desulfurization method used. The purpose of the study was to determine the effectiveness of sulfur fixation in the sludge by dosing the PIX 113 coagulant directly into the feedstock before pumping into the chamber. The results obtained confirmed the effectiveness of the coagulant and provided the basis for conducting further studies using other products based on iron compounds. During the experiment, there were no negative effects of applying the coagulant to the batch just before pumping into the chamber. The positive aspects of sludge supplementation with the tested agent included an increase in biogas production due to a decrease in the H_2S concentration and an improvement in biogas quality parameters – CH_4 and CO_2.

Keywords: ferric coagulant, sulfur, PIX, biogas treatment, hydrogen sulfide.

INTRODUCTION

The biogas created as a result of the fermentation process (from sludge in wastewater treatment plants or substrates in biogas plants) must meet the quality conditions set for the fuel by the manufacturer, before it is fed into cogeneration units. The percentage of biomethane in biogas determines its process suitability and further possibility of use in the process of high-efficiency cogeneration of electricity and heat. The calorific value of biogas with a methane content of 60% (v/v) is estimated at 6.0 kWh/m^3 (22.2 MJ/m^3) of raw material (Piechota and Chmielewski 2017, Ignatowicz et al., 2021). Other sources indicate 15 MJ/m^3 as the lower limit of the calorific value from which biogas should be used for energy purposes (Grzesik 2006). Biogas, in addition to its main components, i.e. methane (CH_4) and carbon dioxide (CO_2), also has hydrogen sulfide (H_2S) formed during the acid phase of the fermentation process, ammonia (NH_3), nitrogen (N_2), oxygen (O_2), volatile organic compounds (VOCs), halogenated organic compounds (Halogens) or volatile silicon compounds (VMSs) commonly referred to as siloxanes (Piechota and Chmielewski 2017; Sour, Balcerzak, and Rezka 2016; Ge et al. 2012). Siloxanes, which are difficult to remove from biogas, as well as hydrogen sulfide, reduce the efficiency of the unit's operation, shorten the interval between periodic inspections and replacements, which, as a result, inflates the costs associated with the unit's operation and reduces its annual availability time (Zarczynski et al. 2015, Lenort et al., 2017). The main components and their percentages in biogas are summarized in Table 1.

Hydrogen sulfide is formed during the acid phase of the fermentation process, as a result of biological decomposition of compounds that

Table 1. The main components of biogas by percentage (Grzesik 2006)

Biogas component	Participation [%]
Methane	50 – 75
Carbon dioxide	25 – 50
Water	2 – 7
Hydrogen sulfide	0 – 2
Nitrogen	0 – 2
Hydrogen	0 – 1
Oxygen	0 – 1
Mercaptans trace elements	0 – 1

contain sulfur in their structure. Significant amounts of sulfur are contained in the wastes in which proteins are present, especially those rich in thiols (melatonin, cysteine, cystine). Hydrogen sulfide can also be formed as a result of the transformation of sulfoxides, sulfonic acids and in the process of biological reduction of sulfates present in the feedstock (Olesienkiewicz 2013; Konieczny 2004).

Desulfurization methods

Most manufacturers of CHP units recommend that the hydrogen sulfide content of the gaseous fuel supplying the generators should be 200-300 ppm (Piechota 2016; Zarczynski et al. 2015; Simson and Kozlowski 2021). Whether such values can be achieved depends primarily on the concentration of hydrogen sulfide before desulfurization and the desulfurization method adopted. In practice, chemical, physical and biological methods are used (Paprota 2011; Zdeb and Pawlowska 2009). All of the available methods have their advantages and disadvantages. Although they are characterized by high efficiency, they require considerable investment (sulfur recovery), generate waste, the disposal or regeneration of which is expensive (turf ore, activated carbon, sorption in chemical solutions), or their exploitation is expensive (e.g., Rectisol process). Hence, it is of utmost importance that the desulfurization method be optimally selected to suit the needs of a particular facility.

Experience shows that in the case of wastewater treatment plants, where biogas production is a "beneficial byproduct" of one of the many unit processes of sludge treatment, rather than a pillar of the facility operation, the concentration of hydrogen sulfide in biogas is strongly linked to the quantity, quality and frequency of the co-digestate received. When the hydrogen sulfide standards in the gaseous fuel are periodically exceeded, and there is no desulfurization plant or the existing desulfurization plant is unable to cope with periodic fluctuations in the hydrogen sulfide load at the plant's input, a simple and effective solution seems to be the supplementation of the feedstock with iron compounds, which will allow the sulfur to be retained in the sludge in the form of insoluble iron (II) sulfide that does not pose operational problems (Czuba and Kmiecik 2011; Piechota and Chmielewski 2017; Konieczny 2004). A mixture of Fe^{2+} and Fe^{3+} salts, as indicated by literature data, is more effective in precipitating sulfide than using each of them separately (Padival, Kimbell, and Redner 1995).

The purpose of the study was to determine the effectiveness of chemical sulfur fixation by dosing the PIX 113 coagulant directly into the feedstock, prior to pumping it into the chamber. The coagulant dosage was to ensure that the H_2S content of the biogas remained stable below 300 ppm, using the same batch of feedstock.

MATERIALS AND METHODS

Model diagram

The experiment was conducted in a digester adapted from the GUNT CE 702 model for anaerobic wastewater treatment. Figure 1 is a block diagram of the digester used for the study.

Model working conditions

The sludge in the chamber and the feedstock fed to the model during the experiment came from the Bialystok Wastewater Treatment Plant. (Simson and Kozlowski, 2021, Ignatowicz et al., 2015) The working conditions of the chamber at the technical scale were tried to reflect the model scale as much as possible. Assumptions:

- Mesophilic digestion process conducted at 38.3°C (± 0.3°C);
- Active/total volume of the chamber: 30 dm^3 / 35 dm^3;
- Retention time: 42 days;
- Agitator speed: 150 rpm;
- Agitator type: propeller-type, 2-level;
- Feeding of raw sludge into the chamber and discharge of digested sludge: single, simultaneous;

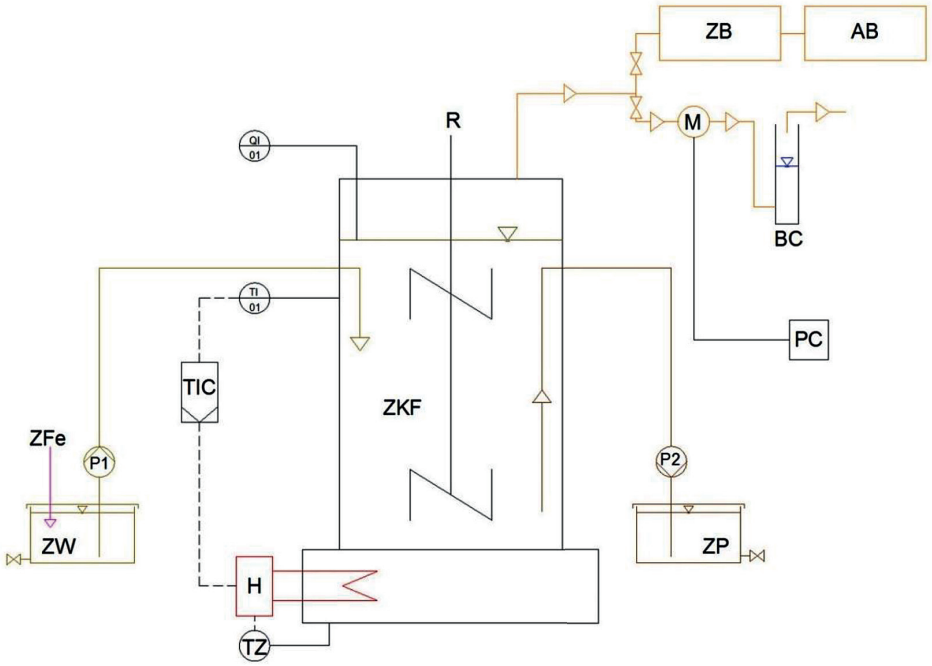

Figure 1. Schematic diagram of the digester model: ZKF – digester, ZW – feedstock tank, ZP – digested sludge tank, ZB – biogas tank, ZFe – Fe-based agent, P1,P2 – pumps, BC – liquid fuse, AB – biogas analyzer, R – stirrer with rpm control, TIC – temperature controller, H – heater, M – biogas flow meter, PC – computer, TZ – thermal protection, TI – temperature measurement, QI – pH measurement

- Sludge was homogenized before being pumped into the chamber with a peristaltic pump;
- Measurement of the amount of biogas produced using a Ritter MGC-1 flow meter;
- Continuous monitoring of pH changes in the chamber;
- Scale of the model relative to the real object: 1: 240 000;
- Analysis of biogas composition in side stream – omission of volume measurement;
- Collection of biogas for analysis: 10 min after pumping a fresh portion of sludge;
- Biogas collection time for analysis: 45 minutes;
- Measurement time: 1 minute;
- Pressure maintained in the gas node (metered): 20 mbar;
- Inspection of biogas parameters for: H_2S, CH_4, CO_2, O_2.

Research methodology

The digestion process was carried out at 38.3°C (± 0.3°C). The feedstock was dosed daily by pumping in 0.7 dm^3 of raw sludge at one time and discharging the same amount of digested sludge at the same time using peristaltic pumps so as not to significantly affect the pressure change in the chamber. Due to the high concentration of hydrogen sulfide in the biogas, a shock dose of 15 g/dm^3 of the formulation was applied at the beginning of the experiment. On subsequent days, efforts were made to reduce the dose, with the final goal of achieving a hydrogen sulfide concentration in biogas of 300 ppm (±10%). The content of nitrogen forms, phosphorus, sulfur, losses on ignition, dry residue, petroleum ether extractables were determined in the raw sludge, digested sludge, while the content of hydrogen sulfide, methane, carbon dioxide and oxygen were determined in biogas. The analytical methodology used is shown in Table 2. (Ignatowicz et al., 2015, Łozowicka et al., 2016, Simson and Kozlowski 2021)

Raw sludge parameters

The parameters that directly affect the amount of biogas produced were studied in the raw sludge, as well as the sulfur content, which translates into hydrogen sulfide content in the produced biogas (Table 3). Taking into account the fact that the commissioning of the model began on 25/01/2022 and the results of the parameters of the sludge used to work the chamber were systematically collected, it should be noted that both the values of substances extracted with petroleum

Table 2. The analytical methods used

Tested medium	Parameter	Standard/Method
Raw sludge	Kjeldahl nitrogen	PN-EN 13342:2002
	Ammonium nitrogen	PN-ISO 5664:2002
	Organic nitrogen	From calculation
	Total phosphorus	PN-EN ISO 6878:2006 + Ap1:2010 + Ap2:2010
	Dry residue	PN-EN 15934:2013-02
	Dry residue roasting losses	PN-EN 15935:2013-02 (reference method)
	Petroleum ether extractables	PB-26 issue 2 dated 01.09.2011
	Sulfur	PN-EN 16170:2017-02
Digested sludge	Dry residue	PN-EN 15934:2013-02
	Dry residue roasting losses	PN-EN 15935:2013-02 (reference method)
	Sulfur	PN-EN 16170:2017-02
Biogas	Hydrogen sulfide	Electrochemical method
	Methane	Method using infrared radiation
	Carbon dioxide	Method using infrared radiation
	Oxygen	Electrochemical method

Table 3. Parameters of raw sludge (input)

Parameter	Unit	Value
Kjeldahl nitrogen	[% d.m.]	2.99
Ammonium nitrogen	[% d.m.]	0.17
Organic nitrogen	[% d.m.]	2.82
Total phosphorus	[% d.m.]	1.23
Dry residue	[% d.m.]	5.2
Dry residue roasting losses	[% d.m.]	80.3
Petroleum ether extractables	[mg/dm^3]	6143 (±1911)
Sulfur	[g/kg d.m.]	14.25

Table 4. Basic parameters of digester model operation

Date	Temperature in the chamber		pH in the chamber
	set	measured	
	[ºC]	[ºC]	[–]
09.03	38.3	38.4	6.9
10.03		38.5	6.9
11.03		38.0	6.8
12.03		38.4	6.8
13.03		38.1	6.8
14.03		38.0	6.8
15.03		38.3	6.8

ether, the content of sulfur, dry matter and the proportion of organic compounds in the input used for the experiment with PIX 113 are higher than the average values from the entire period of operation of the chamber.

RESULTS AND DISCUSSION

Introducing an acidic coagulant (pH<1) directly into the digester, especially at shock doses designed to rapidly reduce the hydrogen sulfide content of the biogas before stabilizing it with a specific dose, carries the risk of depleting the alkalinity buffer and collapsing the digestion process. As indicated by the parameters in Table 4, the process in the digester model was carried out under stable temperature conditions, while the pH of the sludge in the chamber did not change significantly.

The stable performance of the model is also reflected in the high dry organic matter reduction result of more than 60% during the experiment. The final results are summarized in Table 5. Initially, the hydrogen sulfide content of the biogas exceeded 2,000 ppm. A single application of a shock dose of PIX 113 at 15 g/dm^3, and further supplementation with a dose about 40% lower yielded the H_2S content results of 700-800 ppm. Increasing the dose to 12 g/dm^3 resulted in another decrease in concentration, so that a final dose of 9 g/dm^3 caused stabilization of the hydrogen sulfide content in biogas at 300 ppm (±10%).

The effect of the dose of coagulant applied to the feedstock on the amount of hydrogen sulfide in the biogas produced is shown in the graph below (Fig. 2). Since this is a chemical process of sulfur fixation, the result of the application of the agent is visible almost immediately. The increase in the amount of sulfur retained in the digested

Table 5. The results of tests conducted using PIX 113

Data	Dosage amount	Amount of sulfur bound in the sludge	Reduced dry organic matter		Biogas				
					Amount	CH_4	H_2S	O_2	CO_2
	[g/dm³]	[%]	[g/day]	[%]	[dm³/day]	[%]	[ppm]	[%]	[%]
09.03	15	-	12.82	61.40	7.33	54	>2000	0.1	40
10.03	9	56.34	-	-	5.18	55	1055	0.5	38
11.03	7.5	-	17.91	61.27	11.41	54	723	1.0	36
12.03	9	78.05	-	-	17.15	58	833	0.8	33
13.03	12	-	-	-	17.78	60	706	1.2	35
14.03	12	-	17.67	60.46	19.14	60	235	0.8	34
15.03	9	91.82	-	-	20.10	61	329	1.3	32

sludge, and thus the effectiveness of the dosed agent, is shown in the next graph (Fig. 3).

Hydrogen sulfide negatively affects the quality and quantity of biogas produced (Olesienkiewicz 2013). Iron supplementation in the form of co-agulant during the conduct of the experiment caused the concentration of hydrogen sulfide in biogas to decrease from more than 2,000 ppm to

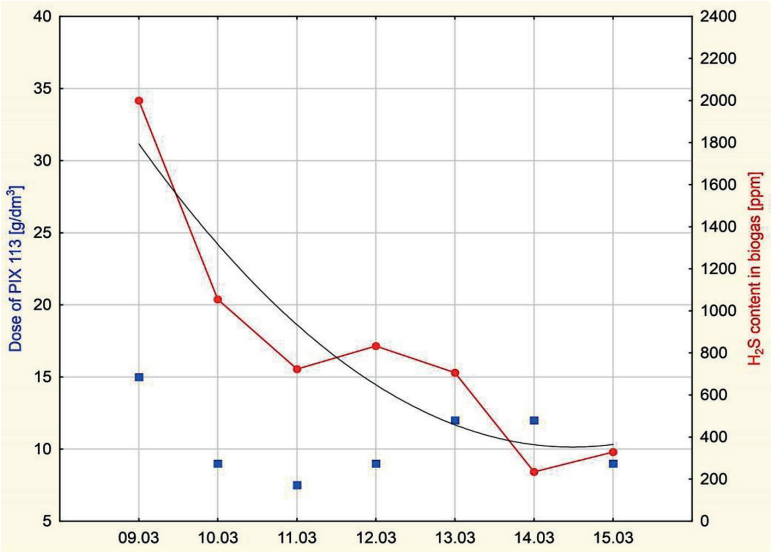

Figure 2. Dependence of the H_2S concentration in biogas on the dose of PIX 113 applied to the batch

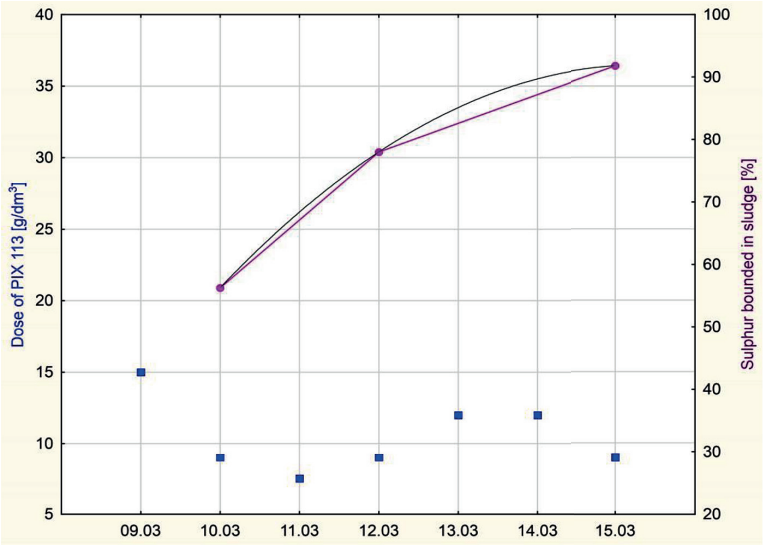

Figure 3. Dependence of the amount of sulfur bound in the sludge on the dose of PIX 113 applied to the batch

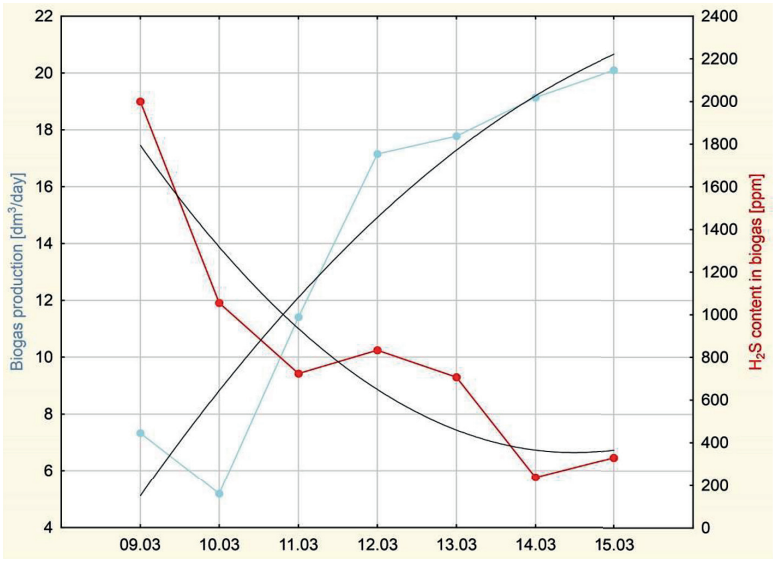

Figure 4. Dependence of the amount of biogas produced on the concentration of hydrogen sulfide in biogas

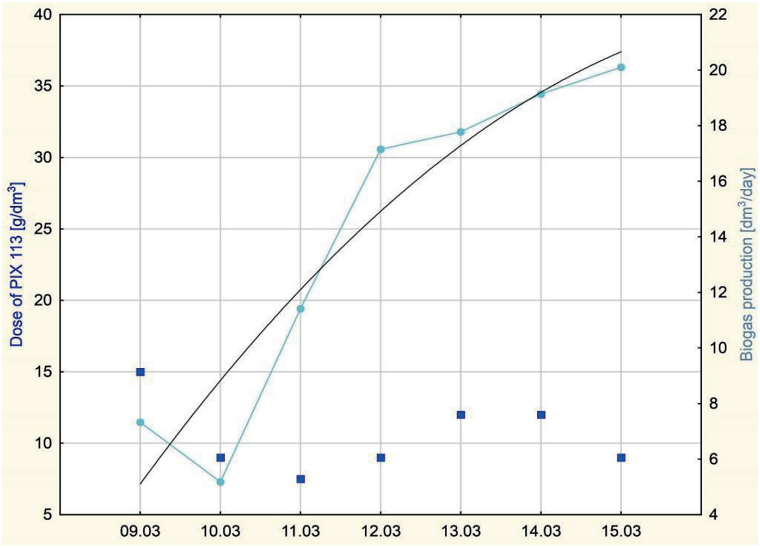

Figure 5. Dependence of the amount of biogas produced on the dose of PIX 113

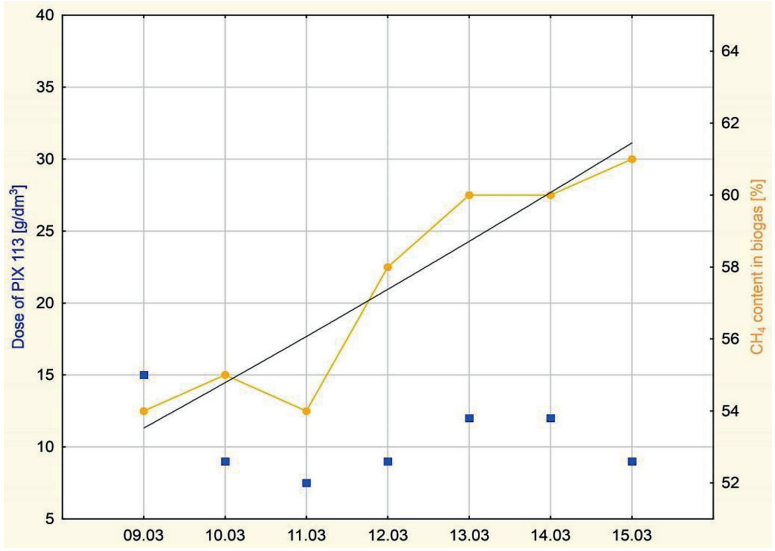

Figure 6. Dependence of the proportion of CH_4 in biogas on the dose of PIX 113

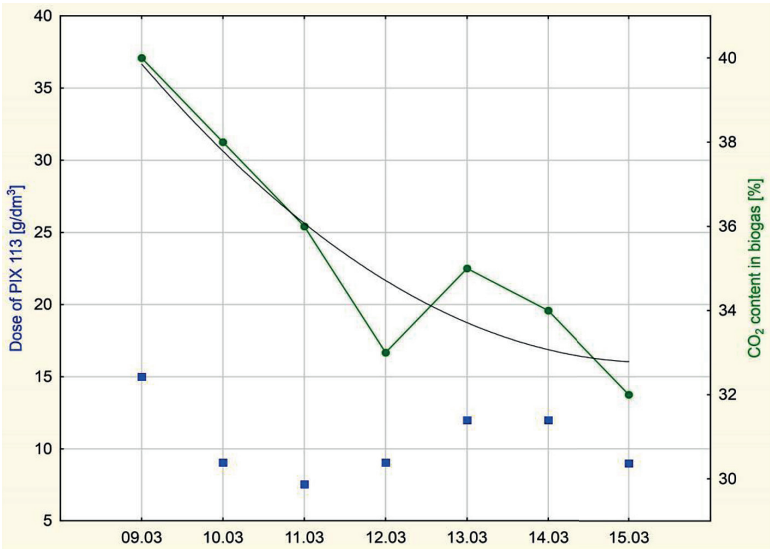

Figure 7. Dependence of the share of CO_2 in biogas on the dose of PIX 113

329 ppm on the last day of the experiment, while biogas production steadily increased (Fig. 4 and Fig. 5). The last recorded daily biogas production was 20.1 dm^3, indicating the high efficiency of the process – more than 1 dm^3 of biogas was obtained from 1 g of dry organic matter removed.

However, the improvement in the quality of the biogas produced as a result of dosing the formulation is indicated by an increase in the proportion of methane (Fig. 6) from 54% to 61% and a decrease in the carbon dioxide content (Fig. 7) of the formulation from 40% to 32%.

CONCLUSIONS

The effectiveness of the PIX 113 coagulant and the method itself indicates the rationale for continuing research with other iron-based chemicals capable of binding sulfur in the sludge, while not exposing the digestion process to breakdown (e.g., by a rapid change in pH) as a result of the applied dose. Supplementation of the feedstock with iron sulfate effectively neutralizes H_2S from biogas, in addition, it promotes further sludge treatment processes: it improves the susceptibility of sludge to dewatering (lower polymer dose, higher dry weight). Low investment costs and relatively easy control of the process make it both an ad hoc method for maintaining the required hydrogen sulfide concentrations in biogas feeding cogeneration units, and a way to effectively support an existing desulfurization plant. Maintaining the parameters of biogas at a stable level that meets the requirements of the manufacturer of a specific CHP unit can significantly reduce the costs incurred due to accelerated wear of operating parts and engine components.

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