LIFE BIOGASNET: Sustainable Biogas Purification System in Landfills and Municipal Solid Wastes Treatment Plants

Biogenic sulfur flocculation from pilot bioscrubber for landfill biogas desulfurization

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10th International Conference on Sustainable Solid Waste Management
21 June 2023, Chania, Crete, Greece

Sandra Torres-Herrera

Position: PhD Student (University of Cádiz)

Education:

- B.Sc. in Biotechnology (University of Cádiz)
- M.Sc. in Agri-food programme (University of Cádiz)

Research interest:

- Effluent gas biofiltration, such as air (VOCs removal) and biogas (desulfurization and upgrading)

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Rbe Reactores biológicos y enzimáticos

BIOGASNET

Introduction

Revalorization of biogas

BIOGAS
45-75% CH_4
20-50% CO_2
10-25% N_2
<1% O_2
500-20.000 ppm_v H_2S
Other compounds

Biogas uses
Renewable energy
Combustion engine
Power generation

H_2S Drawbacks
Toxic
Corrosive
Produce SO_2 (combustion)

Anoxic biodesulfurization

- **Desulfurization widely studied in BTFs**

DRAWBACKS

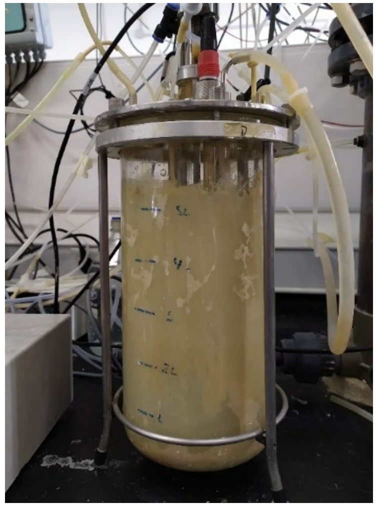
- **Elemental sulfur accumulation**
  - Blockages
  - Technical stop
  - Reinoculation
  - Operating cost increase

- **Sulfate is not desirable because it can be reduced again to H_2S in anaerobic conditions**

Introduction

Anoxic biodesulfurization

Solution? → **Use of suspended biomass bioreactors**



$$5\,HS^- + 2\,NO_3^- + 7\,H^+ \rightarrow 5\,S^0 + N_2 + 6\,H_2O$$

$$S^{2-} + 0.67\,NO_2^- + 2.67\,H^+ \rightarrow S^0 + 0.33\,N_2 + 1.33\,H_2O$$

Allow S^0 recovery

Introduction

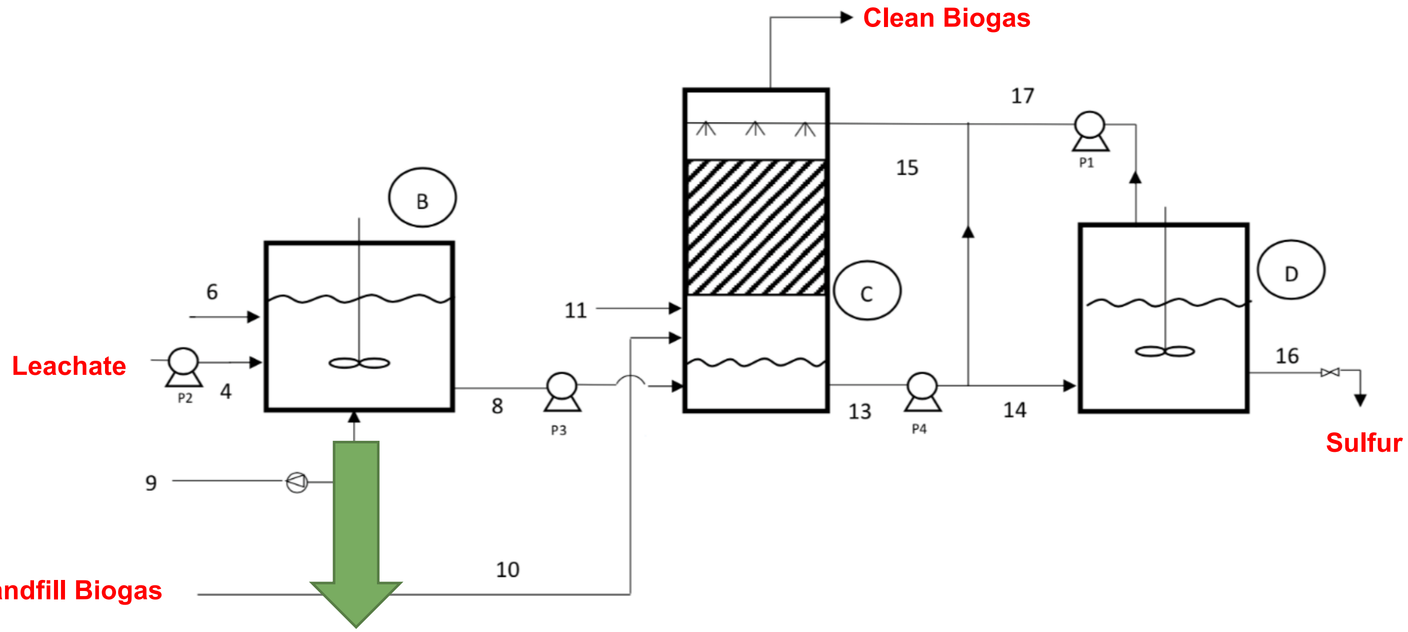
LIFE BIOGASNET: SUSTAINABLE BIOGAS PURIFICATION SYSTEM IN LANDFILLS AND MUNICIPAL SOLID WASTES TREATMENT PLANTS

Main Project Objective

LIFE BIOGASNET European project demonstrates **a new cost-effective and environmental friendly technology for biogas desulfurization based on biological processes**. The project aims to boost the use of biogas as a sustainable energy source and to promote renewable energies production through the **circular economy concept.**

* Prototype installed at the Miramundo-Los Hardales environmental ecopark (Cadiz, Spain)

Nitrification CSTR | Biogas Bioscrubber | Anoxic CSTR



$$NH_4^+(liq) \rightarrow NO_2^-/NO_3^-(liq)$$

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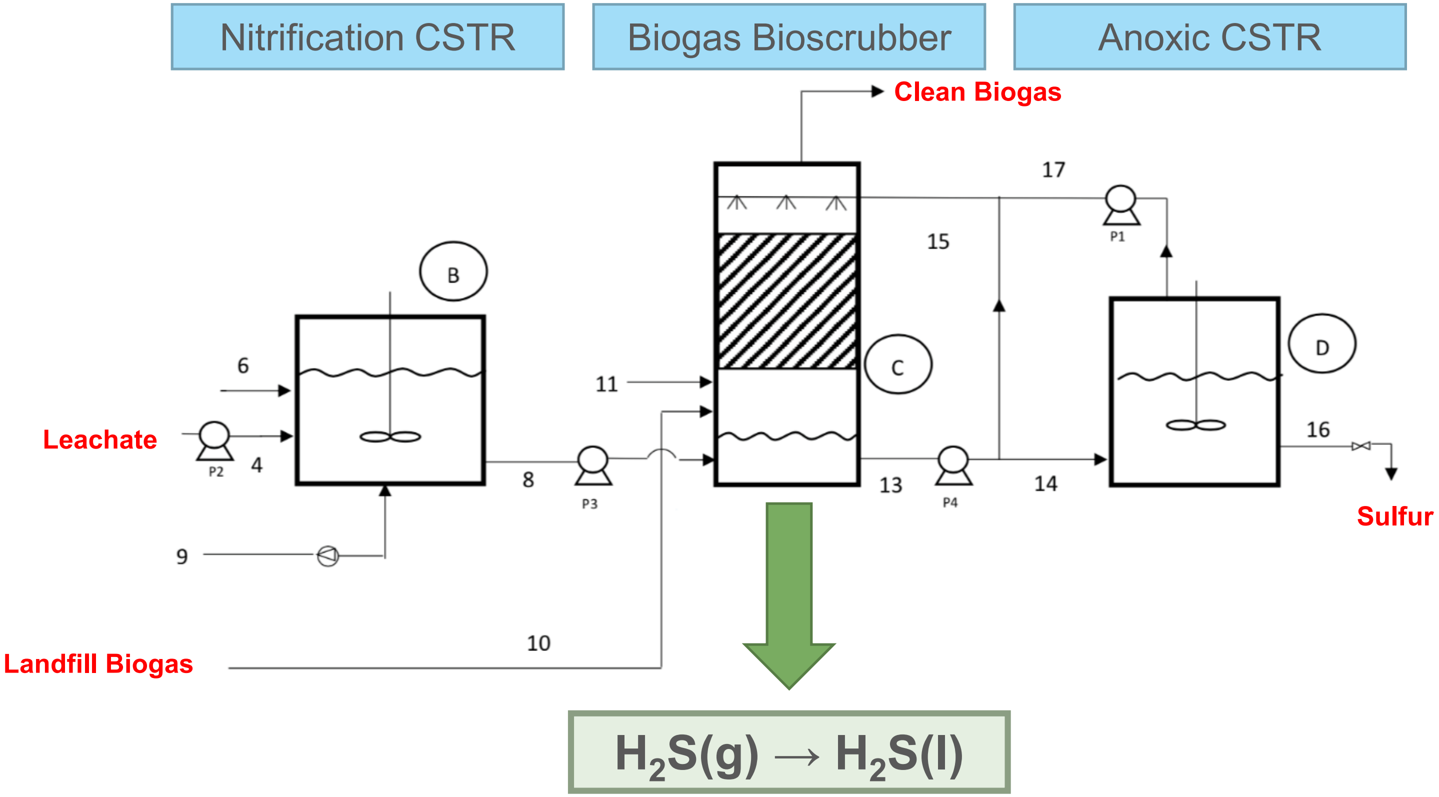

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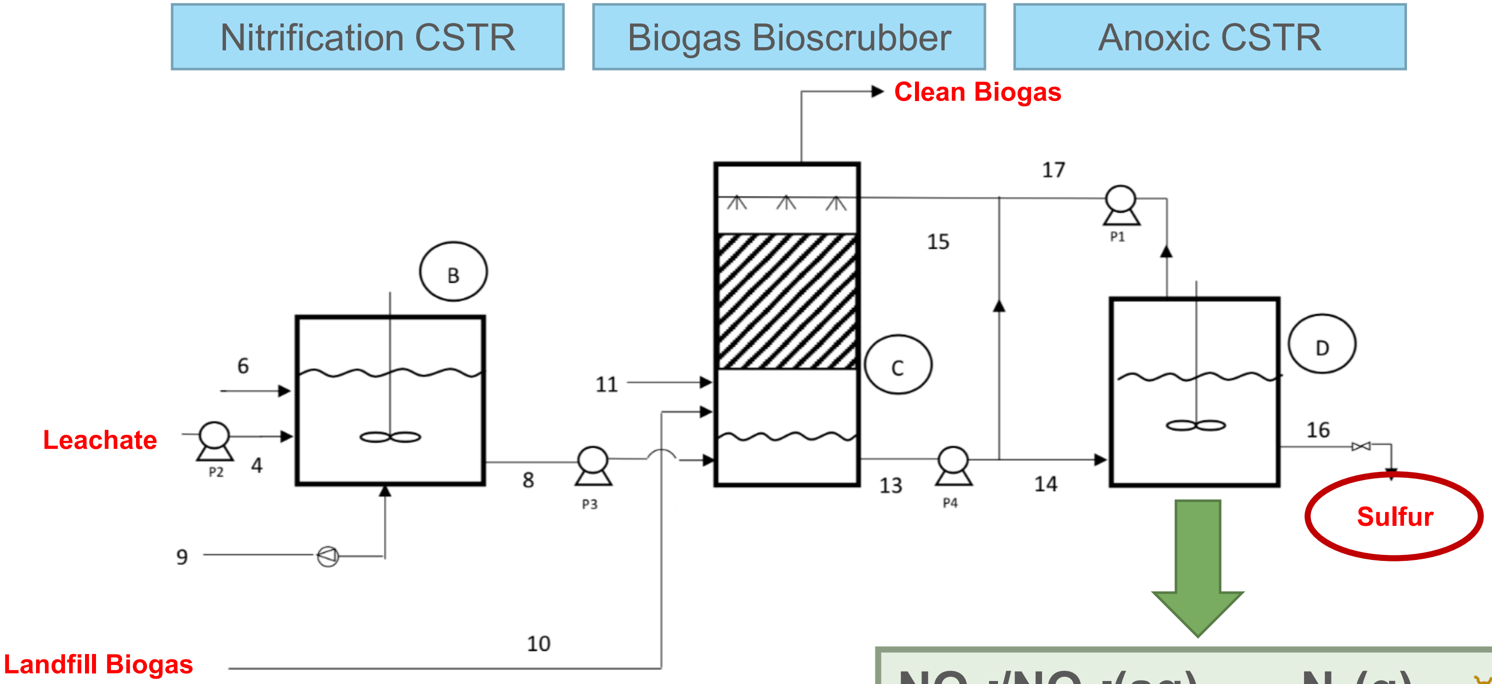

$NO_2^-/NO_3^-(aq) \rightarrow N_2(g)$

$H_2S(l) \rightarrow S^0$ (solid)

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Introduction

Characteristics of sulfur

Chemical sulfur
Non-toxic
Low solubility in water

Biogenic sulfur
Negative charge at pH 8
Particles are hydrophilic
Stable colloidal suspension

→ **Difficulty in settling**

Solution → **Flocculation-coagulation**

Introduction

Sulfur recovery methods

Reagents addition → Coagulation-flocculation → Settling

Factors

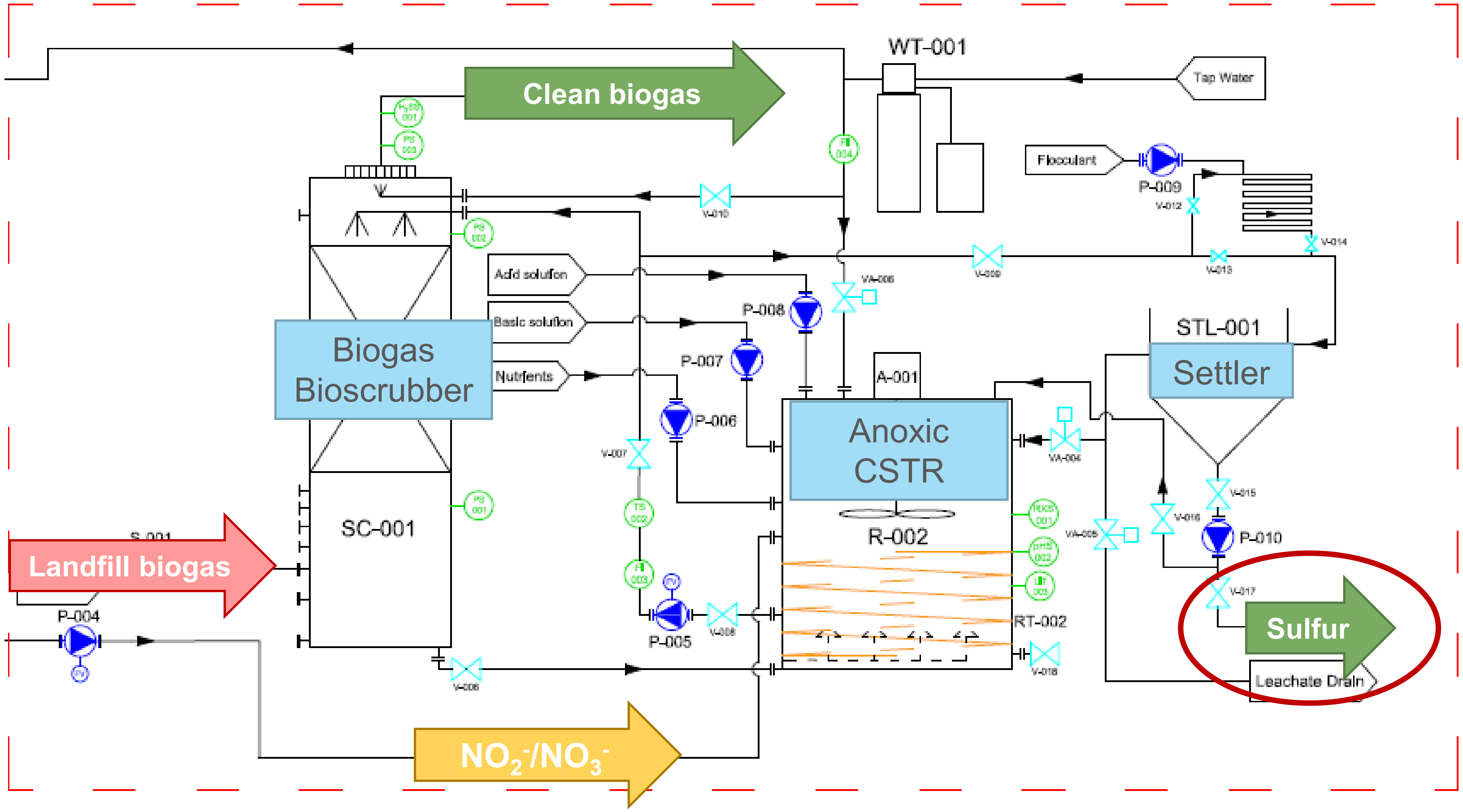
- Flocculant type
- Flocculant dose
- Stirring speed
- Mixing time
- pH
- Temperature

JarTest method

Coagulants	Flocculants
Polyaluminum chloride (PAC)	Polyacrylamide as:
$Al_2(SO_4)_3$	• Anionic
$FeCl_3$	• Cationic
$NaAlO_2$	• Non-ionic

Material and methods

Operating requirements of desulfurization stage



Start-up

100 L of inoculum from STP

Tap water up to 761 L

Nutrients (Na_2CO_3; $NaNO_3$; NH_4Cl and fertilizer)

First stage

Feeding with Na_2S in order to increase the biomass concentration

Long-Term Operation

Landfill Biogas:

$[H_2S]_{in}$ 146.1 ± 54.2 ppm_v

$[O_2]_{in}$ 1.77 ± 0.91%

50 m^3 h^{-1} (nominal value)

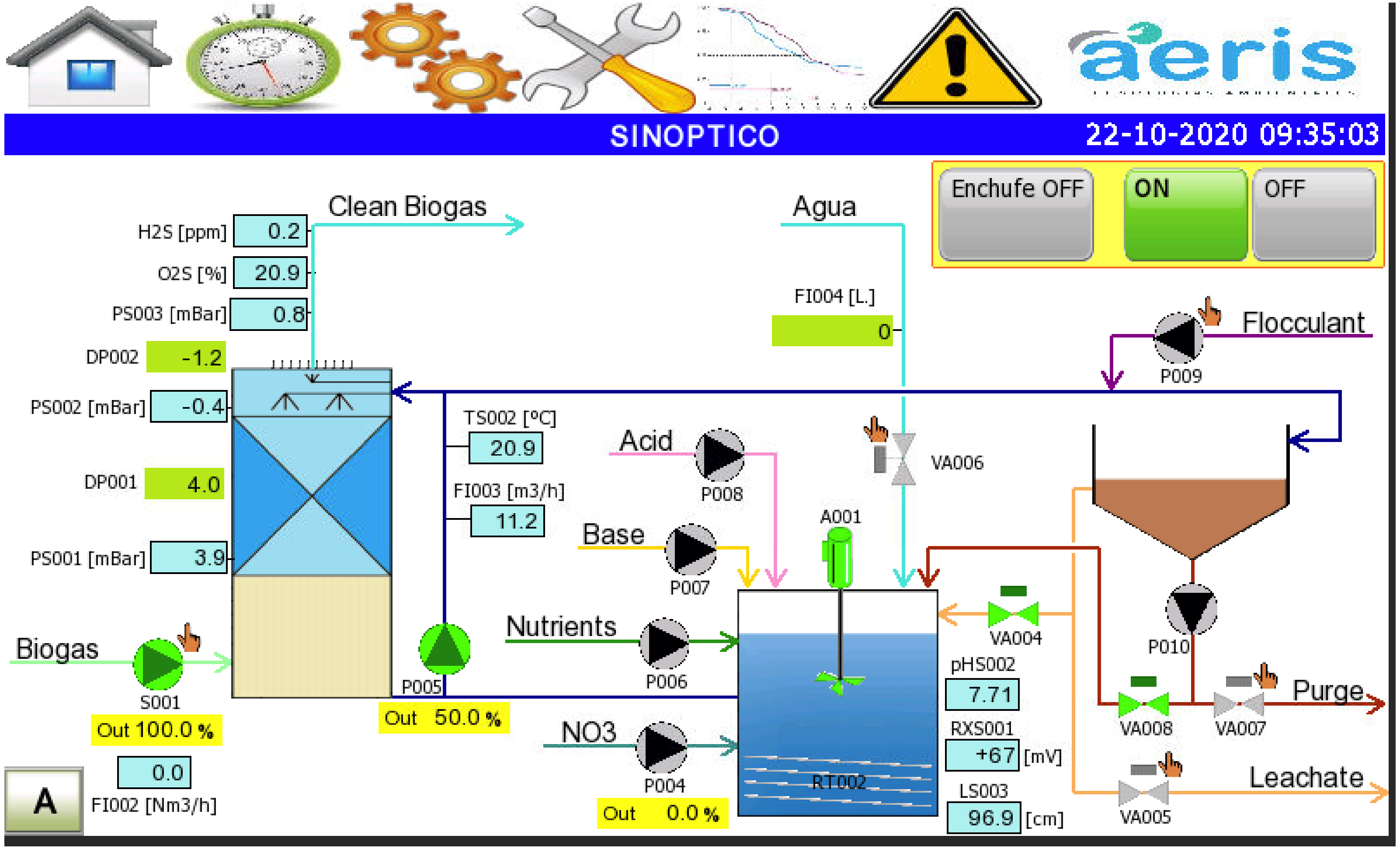
Liquid Nitrified:

Pump on/off

- PID control
- H-L control

Material and methods

Operating requirements of desulfurization stage



Operational parameters:

pH in CSTR

ORP in CSTR

Temperature in CSTR

Level in CSTR

H_2S and O_2 in biogas outlet

Pressure in Bioscrruber

Recirculation flow

Biogas Flow

Material and methods

Flocculation Rate-Jar Test

Step 1 — Initial S^0 solution

Working volume 0.3 L
Temperature 25°C

Sampling for determination of initial S^0 concentration (A_i)

Step 2 — Flocculation and settling S^0

1) Addition of cationic flocculant (Bifloc 690)

Concentrations: 10, 15, 25, 40, 55, 75, and 150 mg L^{-1}

2) 300 rpm
3 min

3) 30-150 rpm
10 min

4) 30 min to settle

Step 3 — Clarified S^0 solution

Sampling for determination of final S^0 concentration (A_f)

Flocculation rate

$$\theta(\%) = \frac{A_i - Af}{A_i} \times 100$$

θ sulfur
θ TSS
θ COD

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*Torres-herrera, S., González-Cortés, J.J., Almenglo, F., Yeste, M.P., Ramírez, M., Cantero, D.: Optimization of biogenic sulfur flocculation from an anoxic desulfurization bioreactor using response surface methodology. Fuel. 323, 124367 (2022). https://doi.org/10.1016/j.fuel.2022.124367

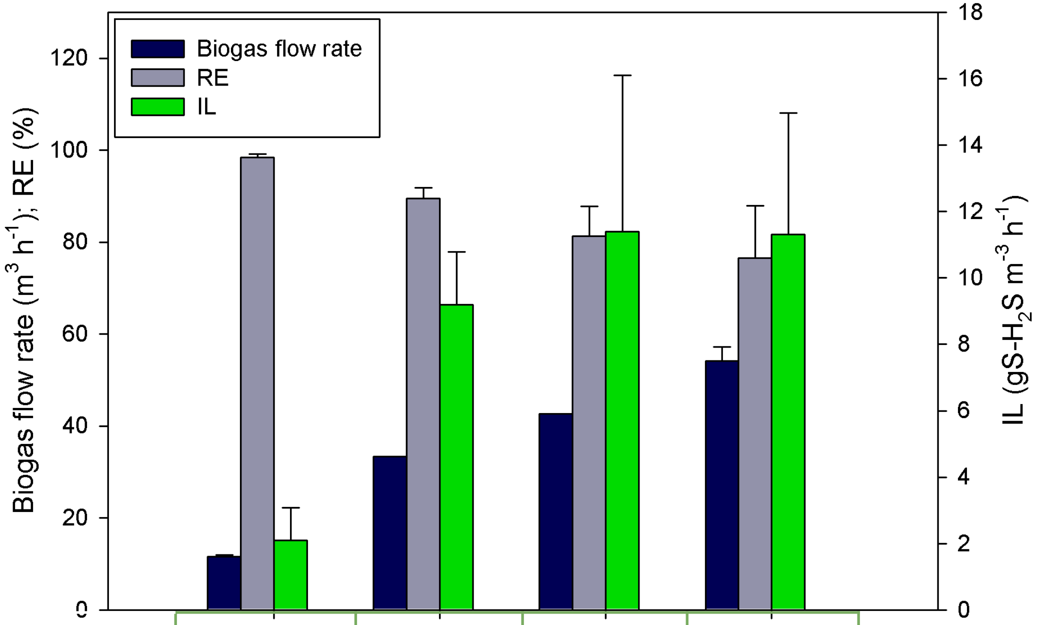
Results and discussion

Long-Term Operation

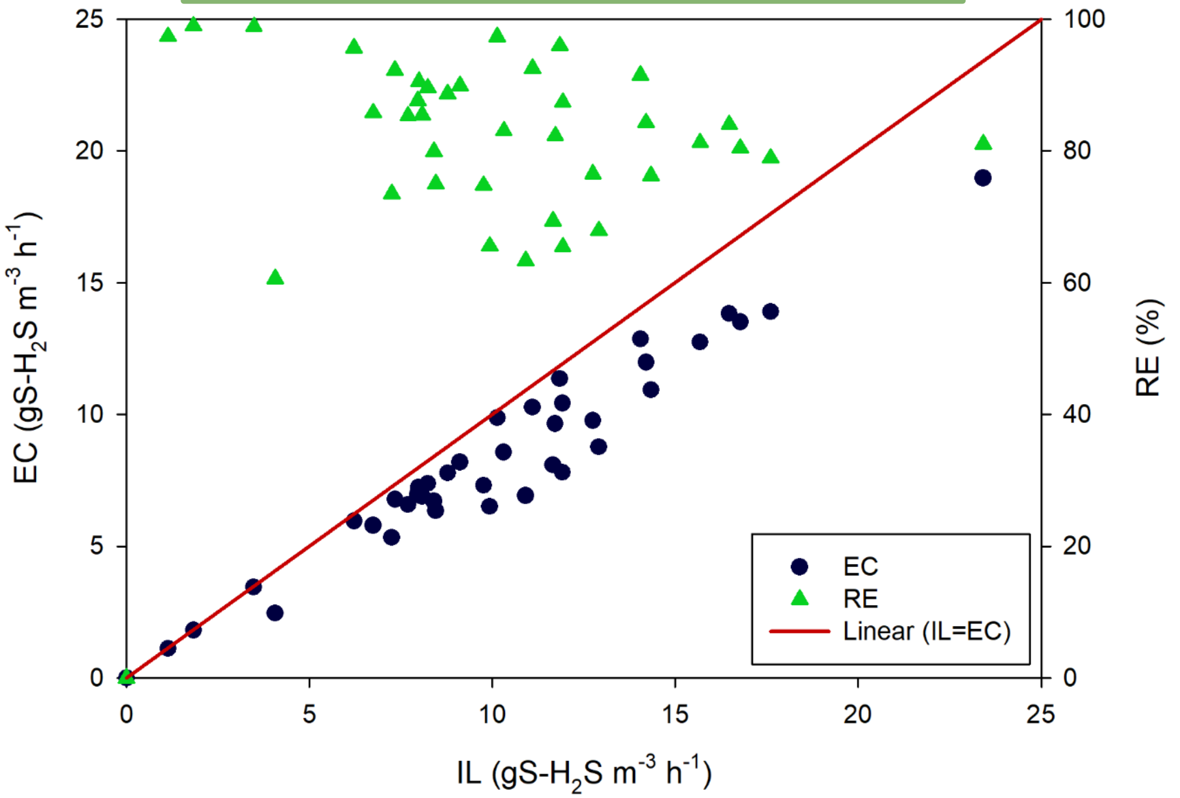
274,801 m^3 of biogas were desulfurized
266 days (38 weeks)
Average biogas flow rate: 43.0 ± 12.2 $m^3\ h^{-1}$

Average EC of 8.4 ± 3.6 $gS\text{-}H_2S\ m^{-3}\ h^{-1}$

RE of 83.0 ± 10.3%.

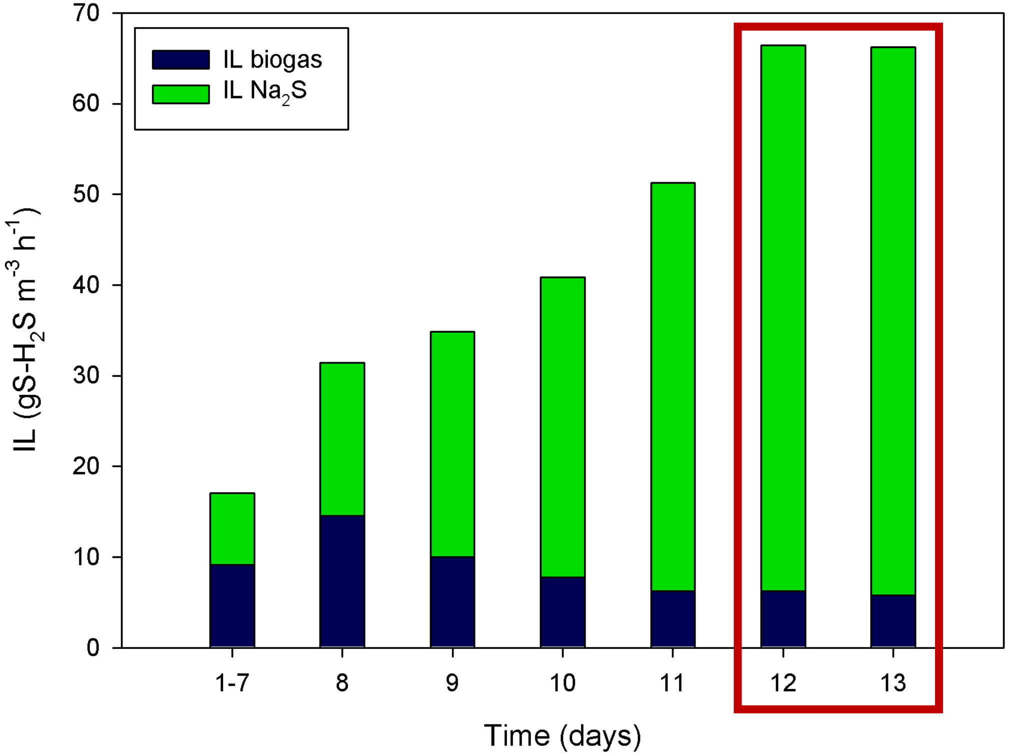


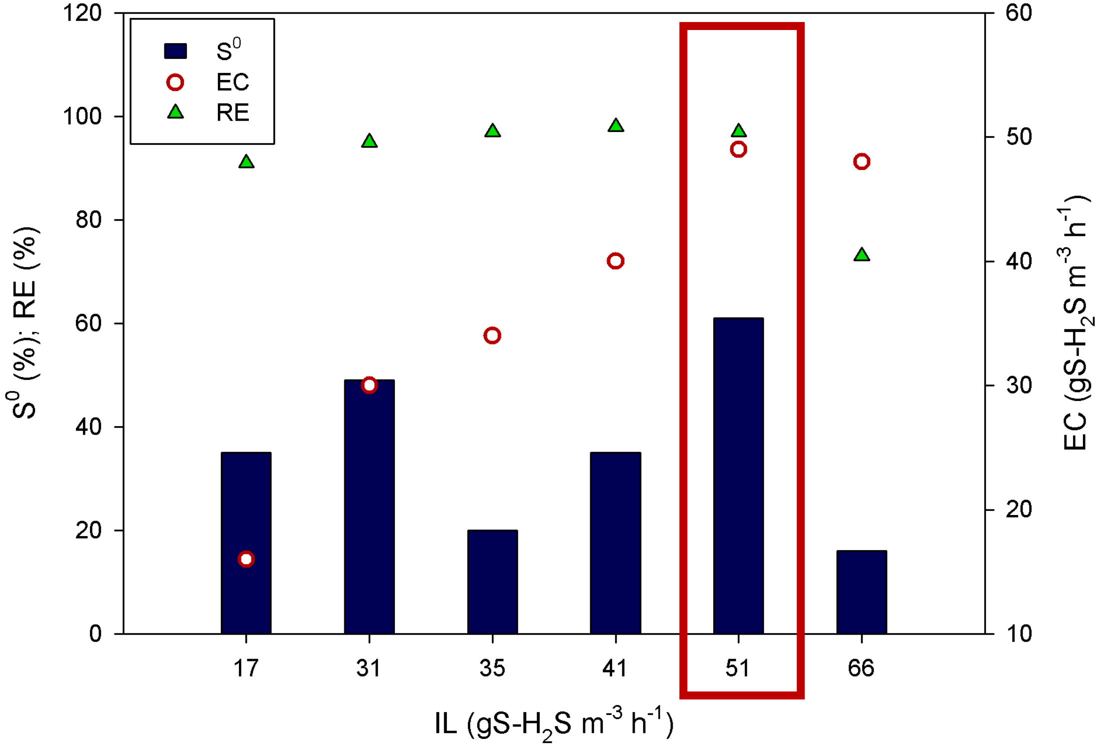
	Week 13-15	Week 16-22	Week 23-41	Week 47-61
Demand of NO_3^- (g)	850	469	292	2



Results and discussion

Test the sulfide removal limits of the system, adding sulfide salt solution.





A maximum IL of 66.4 $gS\text{-}H_2S\ m^{-3}\ h^{-1}$ was reached.

Maximum EC of 49.5 ± 0.6 $gS\text{-}H_2S\ m^{-3}\ h^{-1}$
RE of 96.5 ± 1.1%
Maximum sulfur production of 61%
Nitrate demand: 318 g $N\text{-}NO_3^-$ d^{-1}

Results and discussion

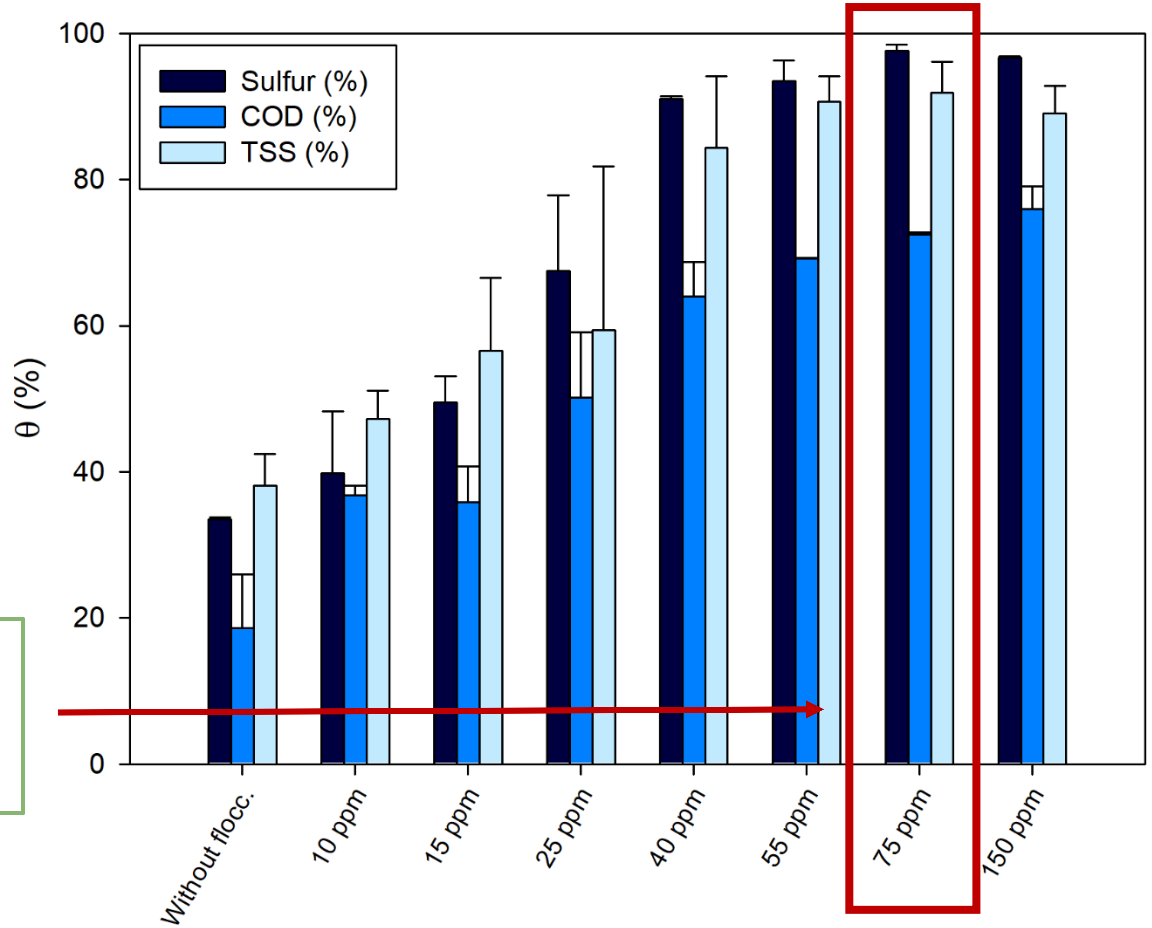
Application of flocculation method

Cationic flocculant
Bifloc 690

300 rpm 3 min
30 rpm 10 min
30 min to settle

Initial sample characteristics
Sulfur = 3,696 ± 77 mg S^0 L^{-1}
COD = 9,574 ± 177 mg O_2 L^{-1}
TSS = 9,633 ± 1,347 mg L^{-1}

θ sulfur = 97.6 ± 0.9%
θ COD = 72.5 ± 0.3%
θ TSS = 91.9 ± 4.2%



Conclusions

- The **desulfurization of real biogas** has been successfully carried out on a pilot-scale standing as a feasible alternative to the current physical-chemical processes.
- **Low H_2S** concentration and **high O_2** concentration at the inlet biogas stream caused a decrease in nitrate demand, leading to **aerobic H_2S oxidation**.
- For an **IL of 51.2 gS-H_2S m^{-3} h^{-1}** (using sodium sulfide), the BIOGASNET technology can reach a maximum **EC of 49.5 ± 5.3 gS-H_2S m^{-3} h^{-1}** and a maximum **RE of 96.5 ± 1.1%.** In these conditions, the value of **sulfur production was 61%**.
- A **flocculation sulfur rate of 97.6 ± 0.9%** was achieved for an initial sulfur concentration of 3,696 ± 77 mg S^0 L^{-1}.

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CHANIA 2023

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Thank you !

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