Biogenic sulfur flocculation from pilot bioscrubber for landfill biogas desulfurization

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

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**Introduction**

Revalorization of biogas

**BIOGAS**
- 45-75% CH₄
- 20-50% CO₂
- 10-25% N₂
- <1% O₂
- 500-20,000 ppmv H₂S
- Other compounds

**Biogas uses**
- Renewable energy
- Combustion engine
- Power generation

**H₂S Drawbacks**
- Toxic
- Corrosive
- Produce SO₂ (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 H₂S in anaerobic conditions**
Anoxic biodesulfurization

Solution?

Use of suspended biomass bioreactors

Allow $S^0$ recovery

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

\[ S^{2-} + 0.67NO_3^- + 2.67H^+ \rightarrow S^0 + 0.33N_2 + 1.33H_2O \]
**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.

\[
\text{NH}_4^+\text{(liq)} \rightarrow \text{NO}_2^-/\text{NO}_3^-\text{(liq)}
\]

* Prototype installed at the Miramundo-Los Hardales environmental ecopark (Cadiz, Spain)
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\[
\text{NO}_2^-/\text{NO}_3^-(aq) \rightarrow \text{N}_2(g) \\
\text{H}_2\text{S}(l) \rightarrow \text{S}^0 \text{ (solid)}
\]

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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

### Coagulants
- Polyaluminum chloride (PAC)
- \( \text{Al}_2(\text{SO}_4)_3 \)
- \( \text{FeCl}_3 \)
- \( \text{NaAlO}_2 \)

### Flocculants
- Polyacrylamide as:
  - Anionic
  - Cationic
  - Non-ionic

**JarTest method**
Material and methods

Operating requirements of desulfurization stage

Start-up
100 L of inoculum from STP
Tap water up to 761 L
Nutrients (Na\textsubscript{2}CO\textsubscript{3}; NaNO\textsubscript{3}; NH\textsubscript{4}Cl and fertilizer)

First stage
Feeding with Na\textsubscript{2}S in order to increase the biomass concentration

Long-Term Operation

Landfill Biogas:
\[ [\text{H}_2\text{S}]_{\text{in}} \, 146.1 \pm 54.2 \text{ ppmv} \]
\[ [\text{O}_2]_{\text{in}} \, 1.77 \pm 0.91\% \]
50 m\textsuperscript{3} h\textsuperscript{-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
- H₂S and O₂ in biogas outlet
- Pressure in Bioscrubber
- Recirculation flow
- Biogas Flow
Material and methods

**Flocculation Rate-Jar Test**

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

\[
\theta = \frac{A_i - A_f}{A_i} \times 100
\]

Results and discussion

Long-Term Operation

274,801 m³ of biogas were desulfurized over 266 days (38 weeks). The average biogas flow rate was 43.0 ± 12.2 m³ h⁻¹.

Average EC of 8.4 ± 3.6 gS-H₂S m⁻³ h⁻¹.

RE of 83.0 ± 10.3%.

Demand of NO₃⁻ (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-H₂S m⁻³ h⁻¹ was reached.

Maximum EC of 49.5 ± 0.6 gS-H₂S m⁻³ h⁻¹
RE of 96.5 ± 1.1%
Maximum sulfur production of 61%
Nitrate demand: 318 g N-NO₃⁻ 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 $\text{H}_2\text{S}$ concentration and high $\text{O}_2$ concentration at the inlet biogas stream caused a decrease in nitrate demand, leading to aerobic $\text{H}_2\text{S}$ oxidation.

• For an IL of $51.2 \text{ gS-}\text{H}_2\text{S m}^{-3}\text{ h}^{-1}$ (using sodium sulfide), the BIOGASNET technology can reach a maximum EC of $49.5 \pm 5.3 \text{ gS-}\text{H}_2\text{S m}^{-3}\text{ h}^{-1}$ and a maximum RE of $96.5 \pm 1.1\%$. In these conditions, the value of sulfur production was 61%.

• A flocculation sulfur rate of $97.6 \pm 0.9\%$ was achieved for an initial sulfur concentration of $3,696 \pm 77 \text{ mg S}^0 \text{ L}^{-1}$. 
LIFE BIOGASNET: Sustainable Biogas Purification System in Landfills and Municipal Solid Wastes Treatment Plants

Thank you!

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