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Bioprocess for simultaneous biogas landfill desulfurization and nitrogen removal from leachate in a pilot plant.

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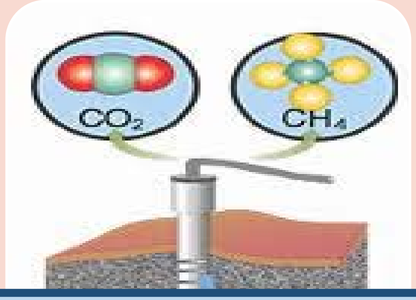
Biogas: renewable energy from organic matter/wastes



Energ
crisis
+
Climat
change
Non-fossil
fuel usage boosting

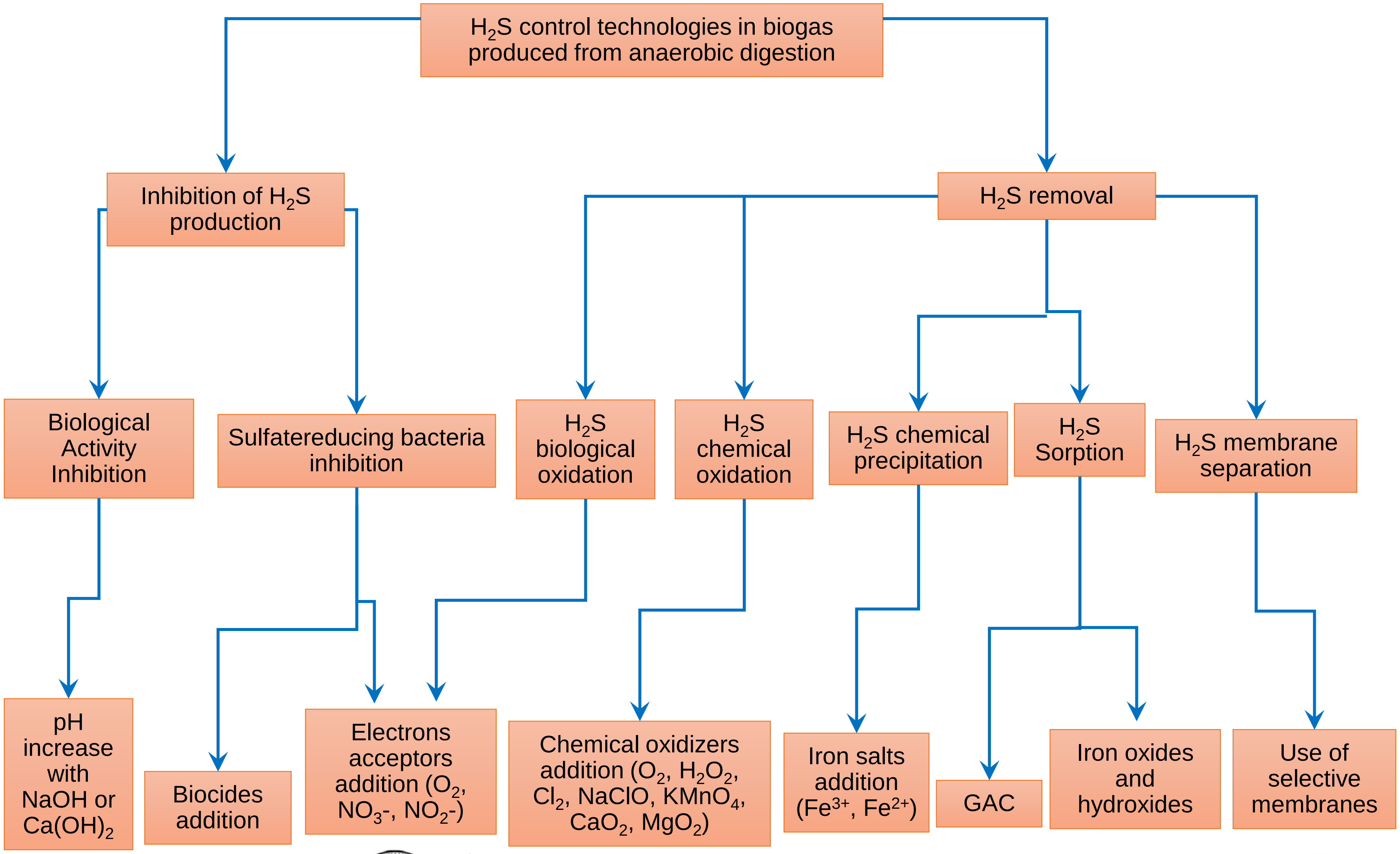
emissions reduction

CH_3SH, VOSCs,
H_2S, …etc.
(1 – 3% v v^{-1})

$_2S$ causes
Acid rain
+
CHP units engines corrosion

A PREVIOUS **DESULFURIZATION** STEP OF BIOGAS IS REQUIRED

Current Desulfurizing Technologies

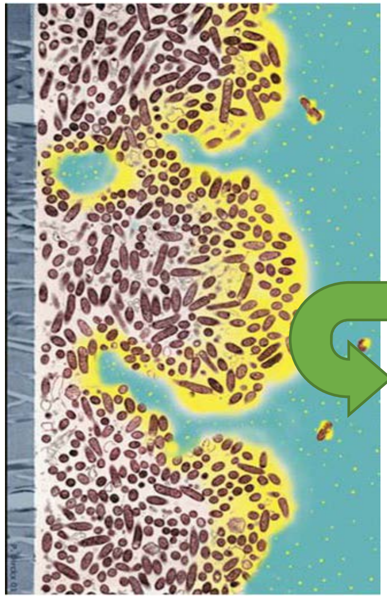


Fundamental of biological techniques: biofilms formation and dynamics

Pollutant or Air toxic + ☺ + O_2 ⇨ Harmless end-products + Biomass

Packing material

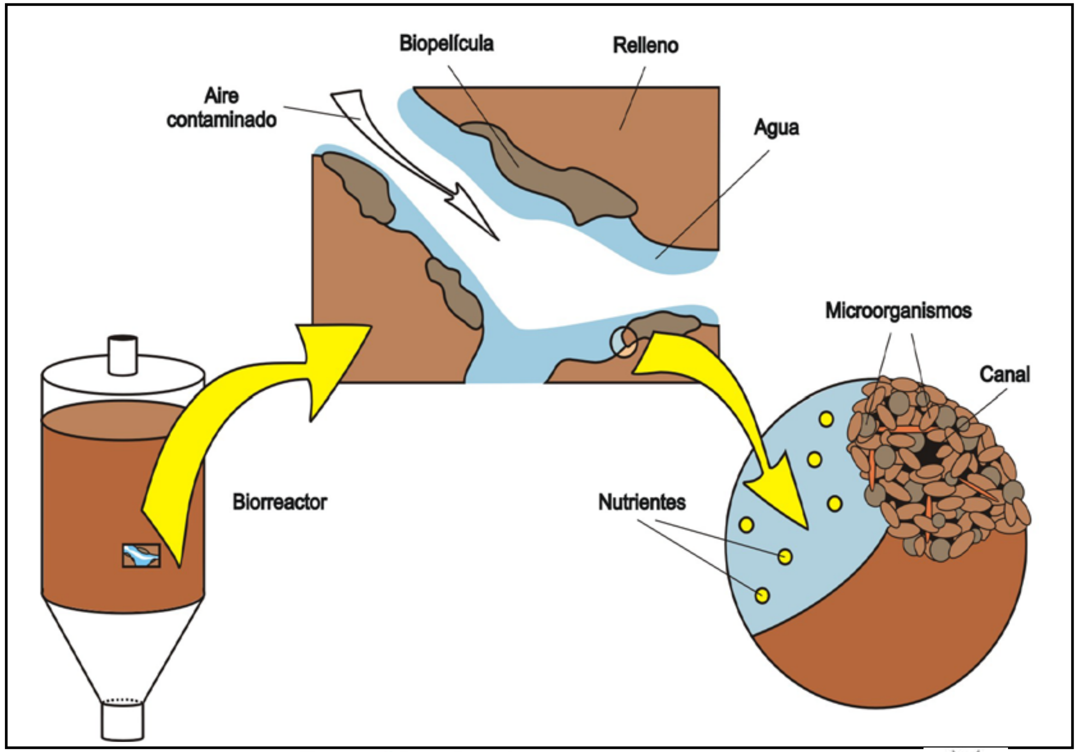
biofilm



Contaminated air

H_2S

Clean air



Biological oxidation of hydrogen sulfide

Reduced Sulfur Compounds (RSC) utilization as electron donors by chemolithotrophic bacteria	
AEROBIC CONDITIONS	**ANOXIC CONDITIONS**
Electron acceptor: Oxygen	Electron acceptor: Nitrate, Nitrite
Electron donors: H_2S, $S_2O_3^{2-}$, Elemental sulfur	Electron donors: H_2S, $S_2O_3^{2-}$, Elemental sulfur
Carbon source: CO_2 **(Plenty of it in biogas!)**	

Reactions involved in aerobic conditions using oxygen (air) as electron acceptor:

$$HS^-_{(aq)} + 0.5\ O_{2\ (aq)} \rightarrow S^0_{(s)} + OH^-_{(aq)}$$

$$S^0_{(s)} + 3/2\ O_{2(aq)} + H_2O \rightarrow SO_4^{2-}{}_{(aq)} + 2H^+_{(aq)}$$

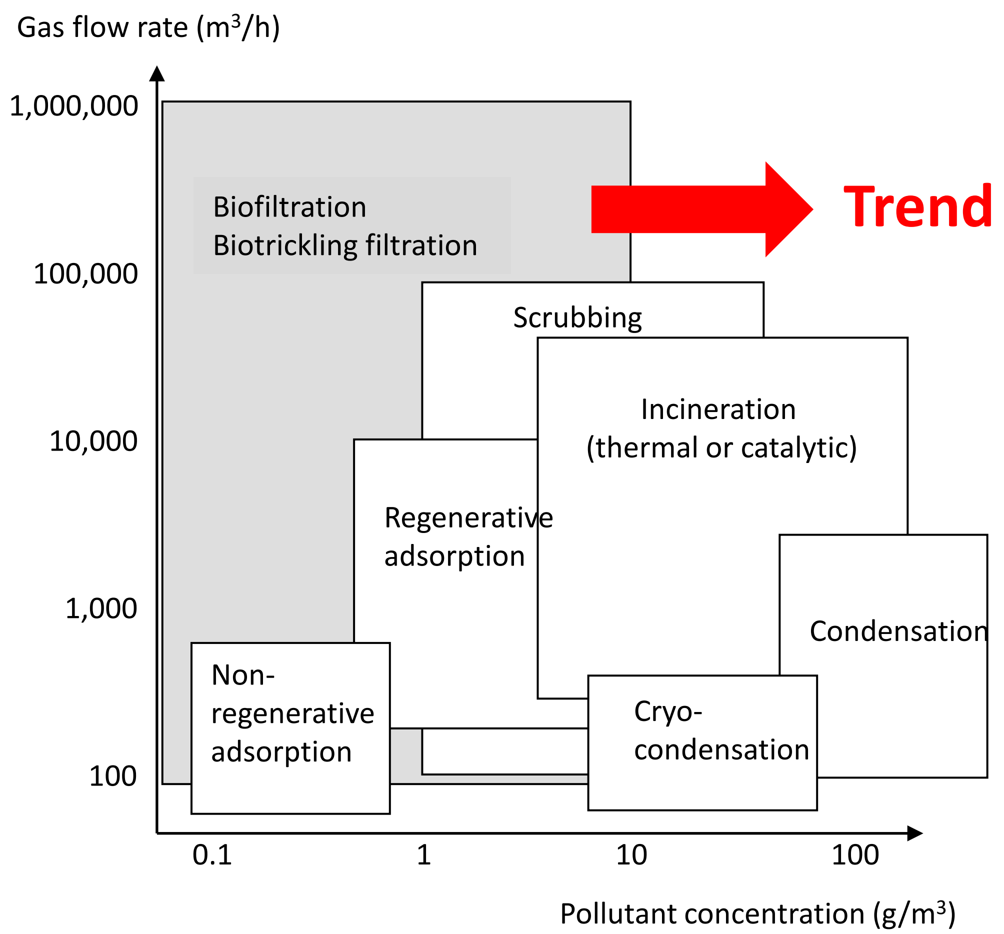
$$HS^-_{(aq)} + 2\ O_{2\ (aq)} \rightarrow SO_4^{2-}{}_{(aq)} + H^+_{(aq)} \quad \text{(Overall)}$$

Biological processes are THE alternative ?

BIOLOGICAL TREATMENT:

- Simple
- No chemicals: Reduced risks
- Economical
- Pollutant degradation produces non-harmful compounds
- Capability to treat large gas flowrates

Challenge: H_2S Concentration in biogas exceeds the Technology limits

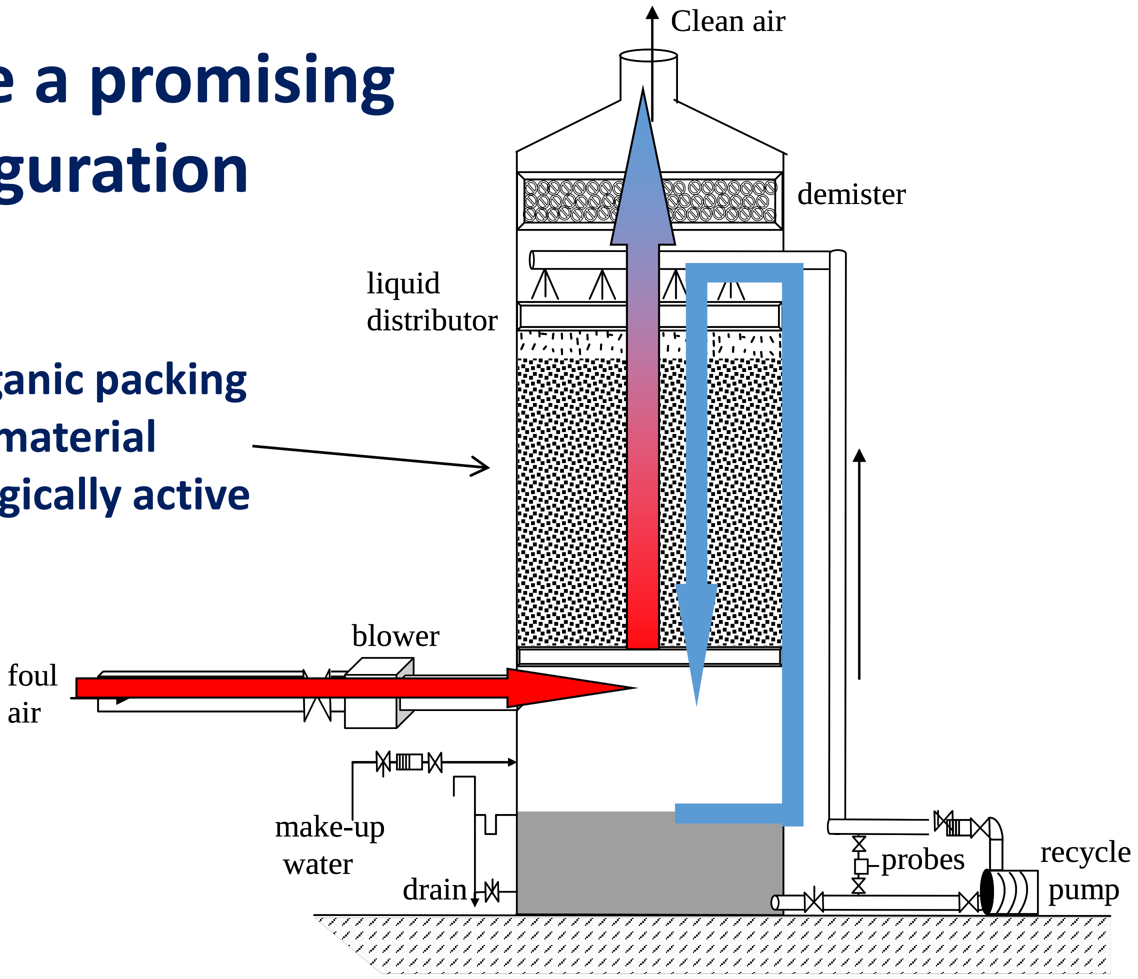


Biological processes are THE alternative ?

Biotrickling filters are a promising bioreactor configuration

Inorganic packing material
Biologically active

- **Plug-flow type bioreactor**
- **Electron acceptor (O_2) supply needed for biogas desulfurization**
- **G-L mass transfer is a key process**



Schematic of a biotrickling filter

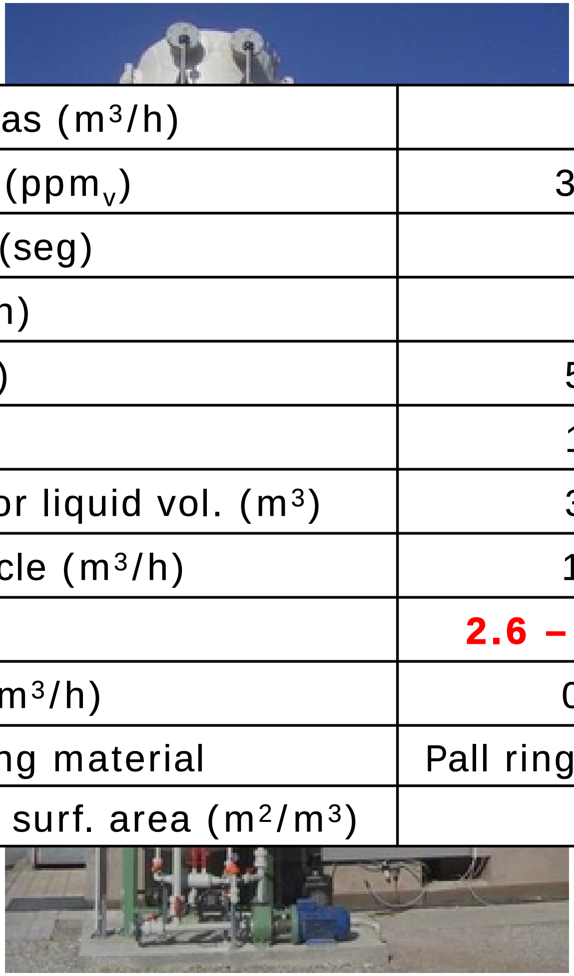
Biogas desulfurization: experiencies from lab-scale to full-scale

A range of designs, operational conditions and strategies have been tested

H_2S_{in} (ppm_v)	EC_{max} ($g\ H_2S\ m^{-3}h^{-1}$)	$O_{2supplied}$	$S\text{-}SO_4^{2-}$/ $S\text{-}H_2S_{removed}$ (%)	pH	Packing	G/L flow pattern	
8000	190	Gas pipe	12	6	HD-Qpack structured	Counter current	*Fortuny et al, 2008, Chemosphere*
8000	175	Gas pipe	clogging	6	PUF	Counter current	*Fortuny et al, 2008, Chemosphere*
8000	201	Diffuser	57	6.5	HD-Qpack structured	Counter current	*Montebello et al, 2010, CEJ*
8000	223	Diffuser	56	2.5	Pall rings	Counter current	*Montebello et al, 2014, JHazMat*
2500	72	Difusser	52	1.9	Pall rings	Co+Counter current	*Rodríguez et al, 2014, PSEP*
2500	54	Jet-venturi	61	1.7	Pall rings	Co+Counter current	*Rodríguez et al, 2014, PSEP*
8000	212	Diffuser	52	6.5	Pall rings	Cocurrent	*López et al., in prep*

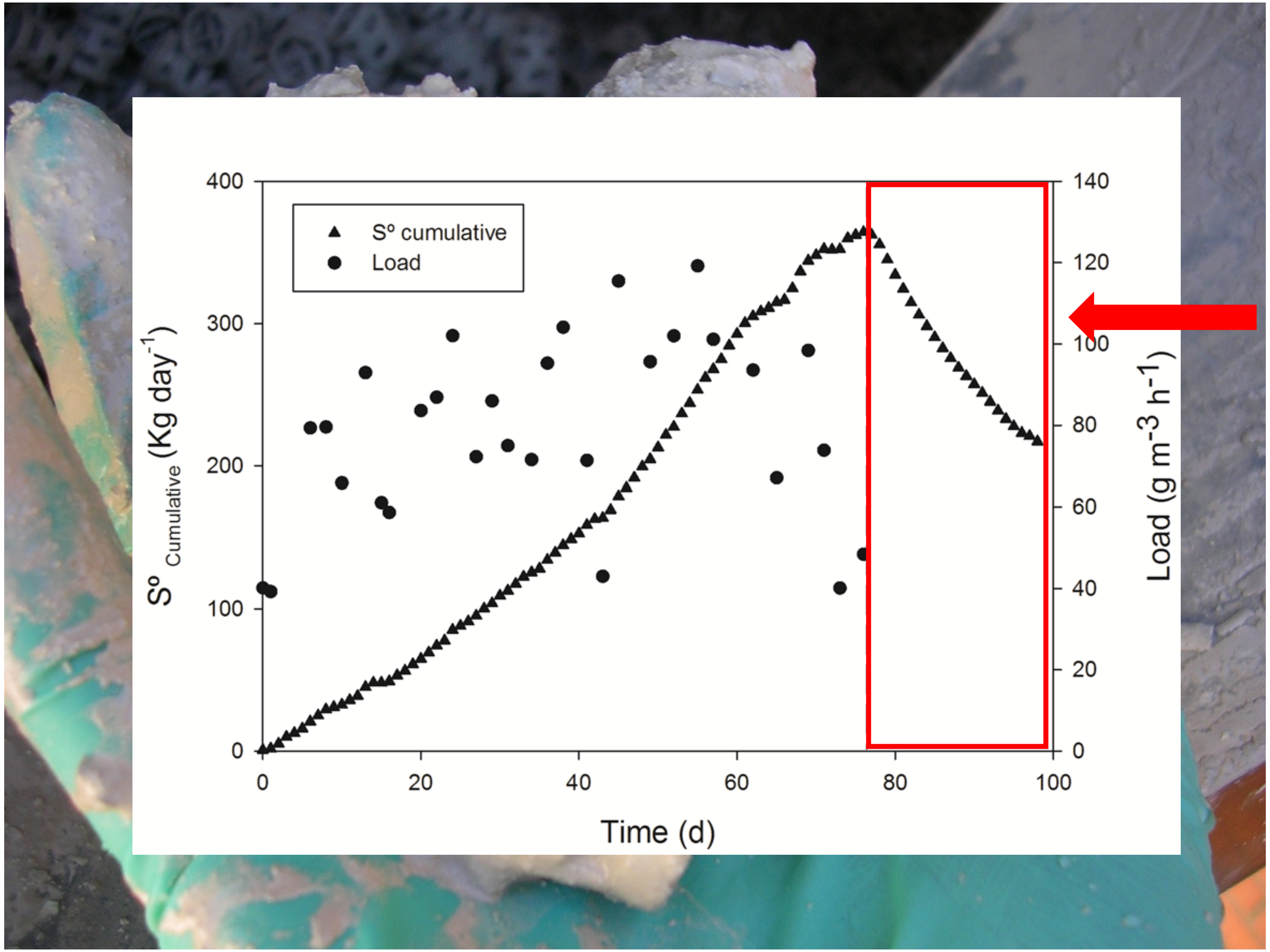
Biogas desulfurization: experiencies from lab-scale to full-scale

Anaerobic digestion facility at Manresa (Barcelona) WWTP



F biogas (m^3/h)	80
[H_2S] (ppm_v)	3000
EBRT (seg)	180
HRT (h)	35
V (m^3)	5,15
D (m)	1,40
Reactor liquid vol. (m^3)	3,00
Qrecycle (m^3/h)	1-10
pH	**2.6 – 2.7**
Qair (m^3/h)	0-20
Packing material	Pall rings 1”
Spec. surf. area (m^2/m^3)	209

But sometimes "things" do not behave as expected…



Biological oxidation of S^0

An alternative to aerobic oxidation: Anoxic desulfurization

Aerobic

$$H_2S + 0.5O_2 \xrightarrow{microorganisms} S^0 + H_2O$$

$$H_2S + 2O_2 \xrightarrow{microorganisms} SO_4^{2-} + 2H^+$$

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Anoxic (total denitrification)

$$H_2S + 0.4NO_3^- + 0.4H^+ \xrightarrow{microorganisms} S^0 + 0.2N_2 + 1.2H_2O$$

$$H_2S + 1.6NO_3^- \xrightarrow{microorganisms} SO_4^{2-} + 0.4H^+ + 0.8N_2 + 0.8H_2O$$

$$S^0 + 1.2NO_3^- + 0.4H_2O \xrightarrow{microorganisms} SO_4^{2-} + 0.8H^+ + 0.6N_2$$

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- No more G-L mass-transfer limitations!
- No comburent (O_2) added to methane
- A N-source is needed

Anoxic desulfurization pilot plant developed by UCA

BIOGASNET

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

https://biogasnet.eu/

OBJECTIVE

Main Project Objective:

BIOGASNET project will demonstrate cost-efficient, low-carbon footprint technologies for biogas upgrading in order to boost the use of biogas as sustainable energy source, to reduce the carbon footprint of the energy cycle and to promote the circular economy.

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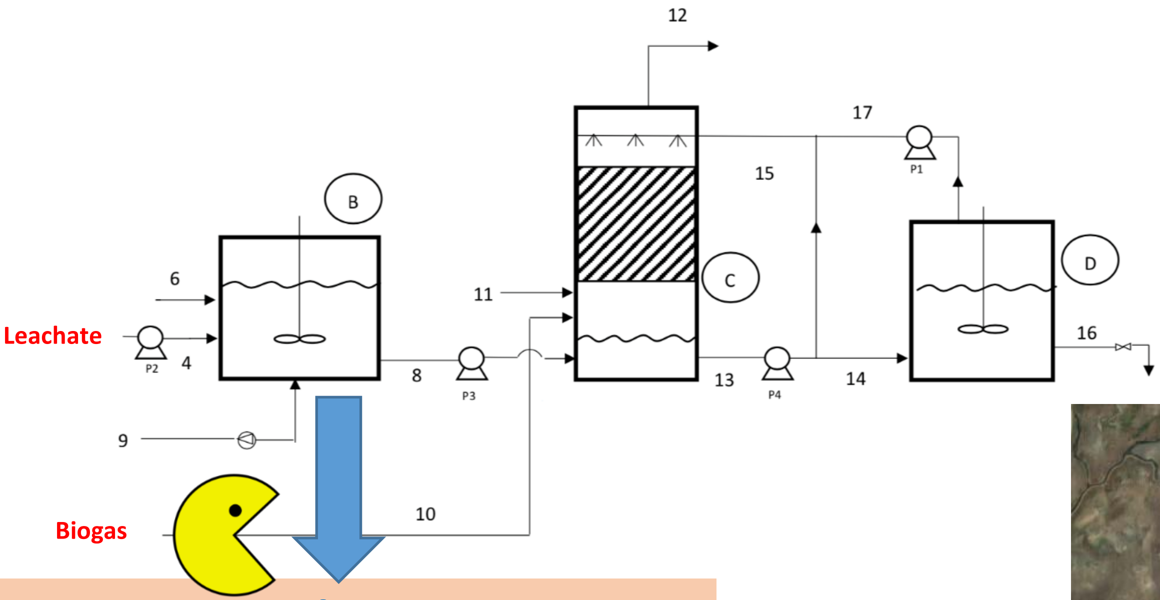
TECHNOLOGY DESCRIPTION

CADIZ Site

Equipment	Description
B	Nitrification CSTR
C	Biogas Scrubber
D	Anoxic CSTR. Sulphur production



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

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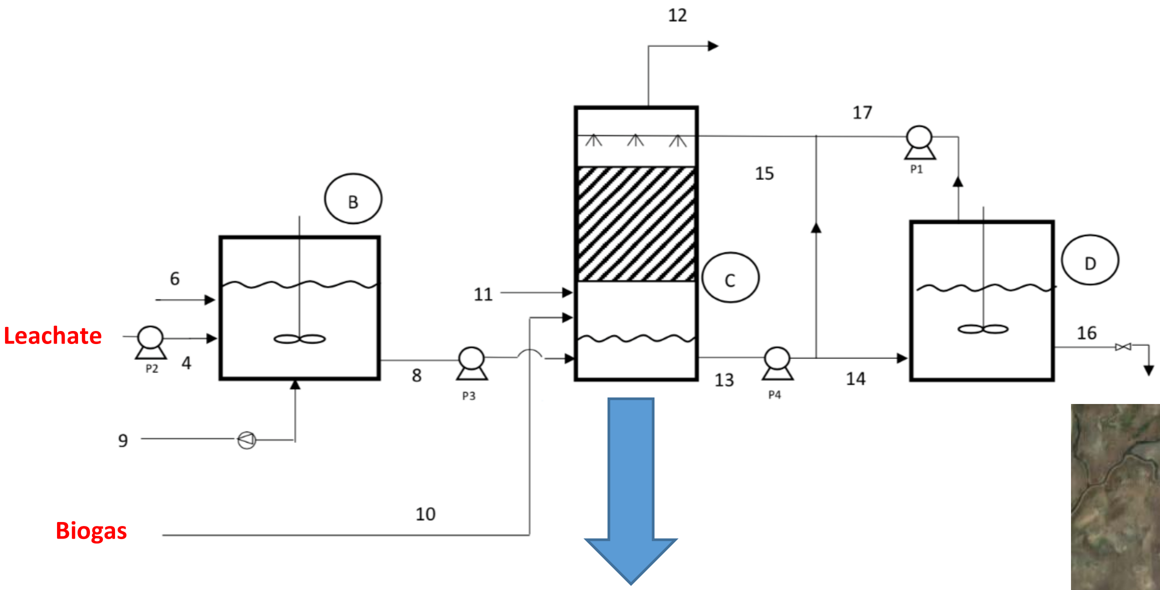

$H_2S(g) \rightarrow H_2S(l)$

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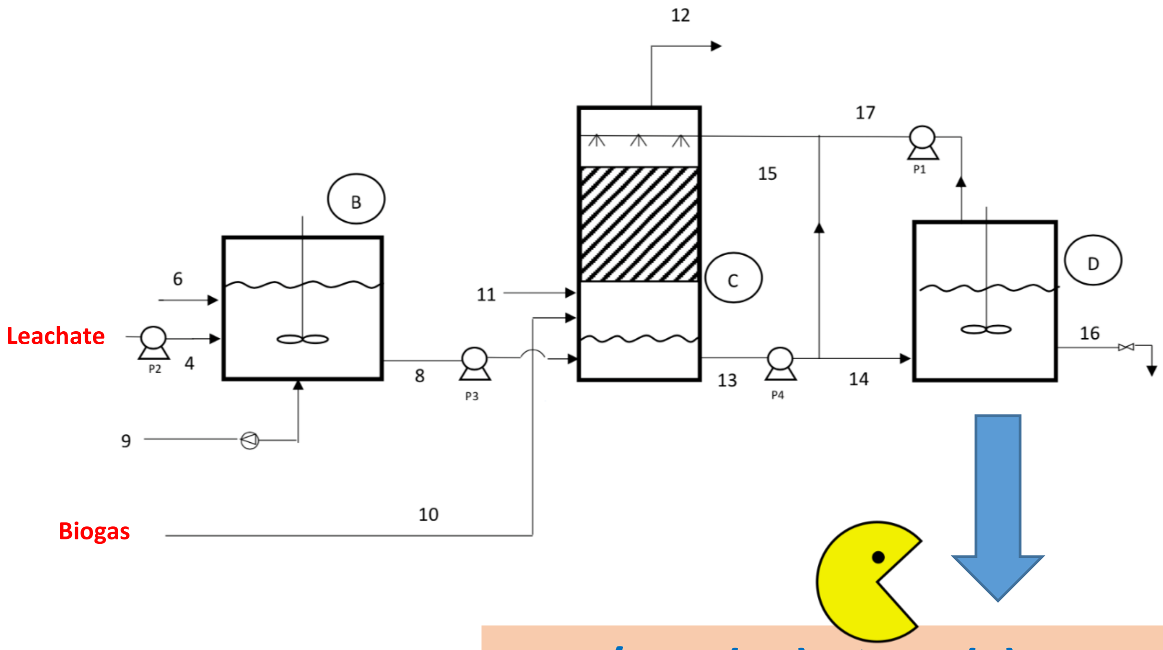


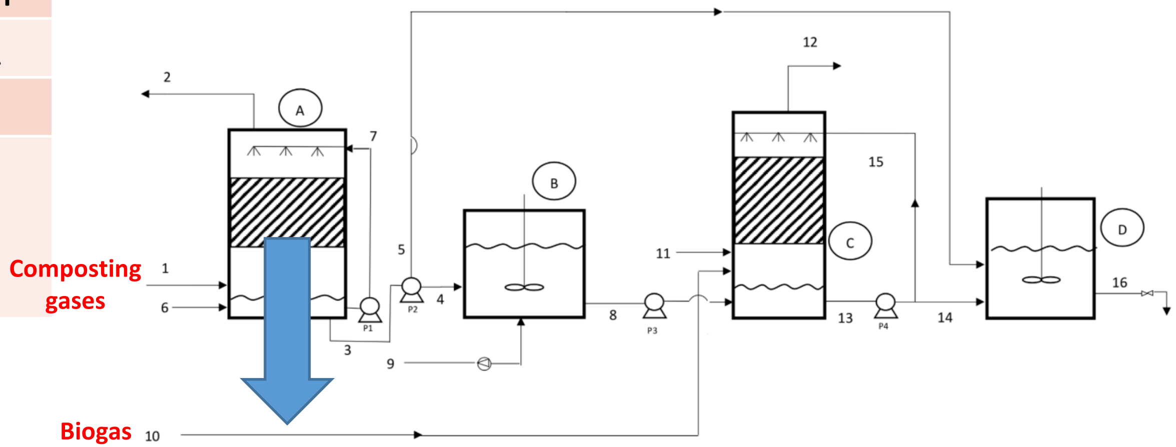
$NO_2^-/NO_3^-(aq) \rightarrow N_2(g)$

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

TECHNOLOGY DESCRIPTION

ATHENS Site

Equipment	Description
A	Ammonia Srubber
B	Nitrification CSTR
C	Anoxic BTF
D	Ammonium sulphate production CSTR



Athens Site (Fili-Ano Liosia MSWTP)

$$NH_3(g) + H_2O \leftrightarrow NH_4OH(liq)$$

TECHNOLOGY DESCRIPTION

ATHENS Site

Equipment	Description
A	Ammonia Srubber
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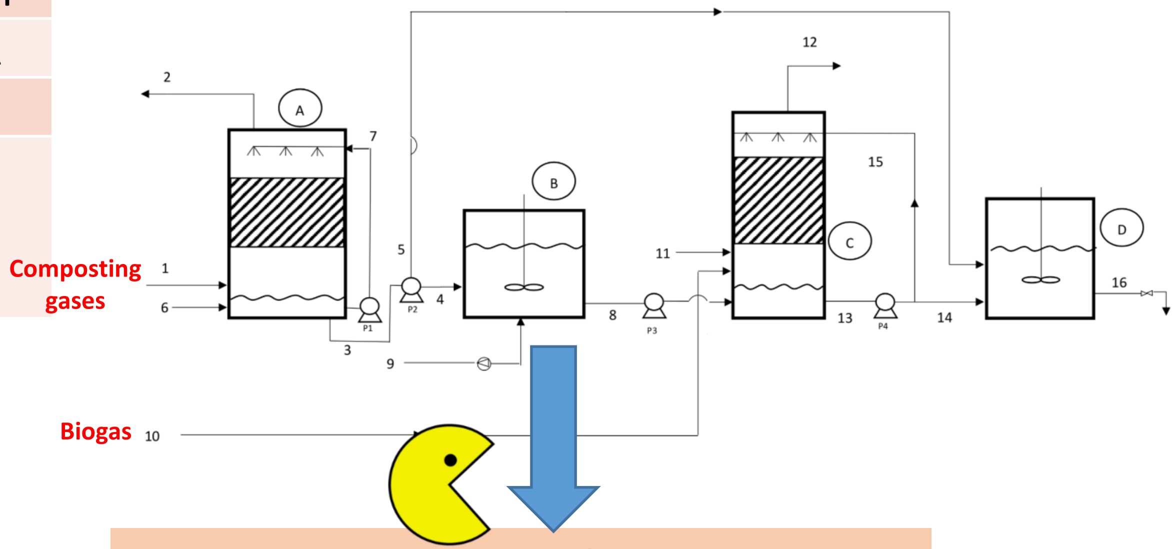

$NH_4OH(liq) \rightarrow NO_2^-/NO_3^-(liq)$

Athens Site (Fili-Ano Liosia MSWTP)

TECHNOLOGY DESCRIPTION

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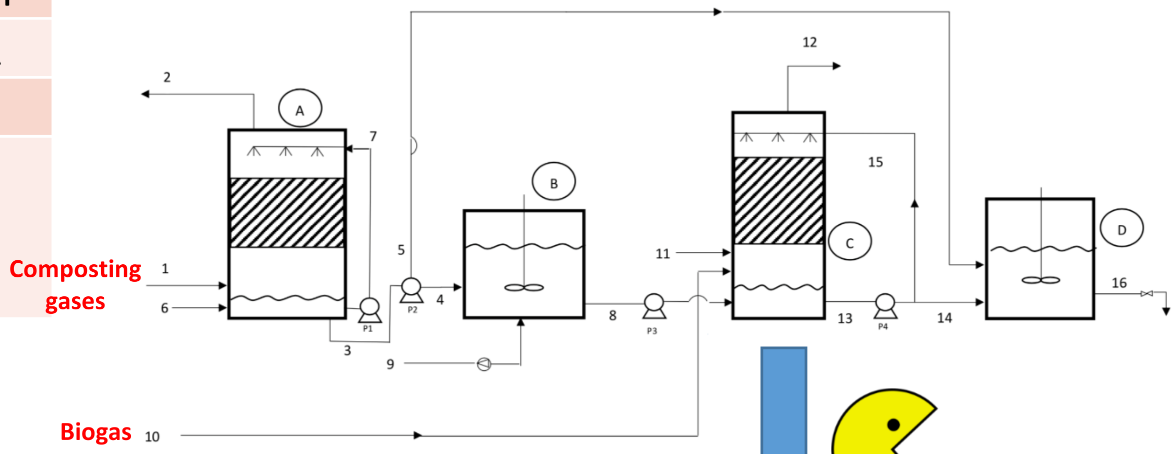

$NO_2^-/NO_3^-(liq) \rightarrow N_2(g)$

$H_2S(g) \rightarrow S^0 \rightarrow SO_4^{2-}(liq)$

Athens Site (Fili-Ano Liosia MSWTP)

TECHNOLOGY DESCRIPTION

ATHENS Site

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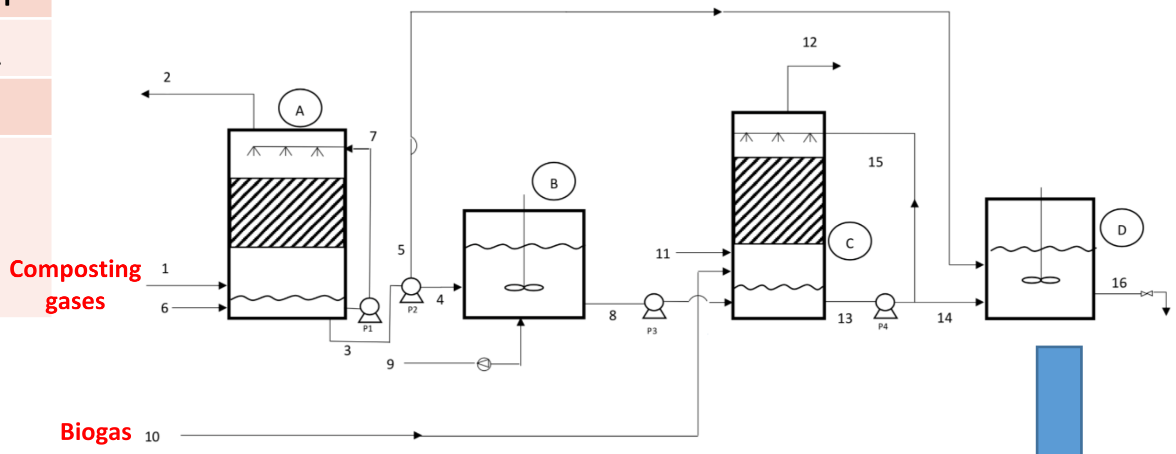
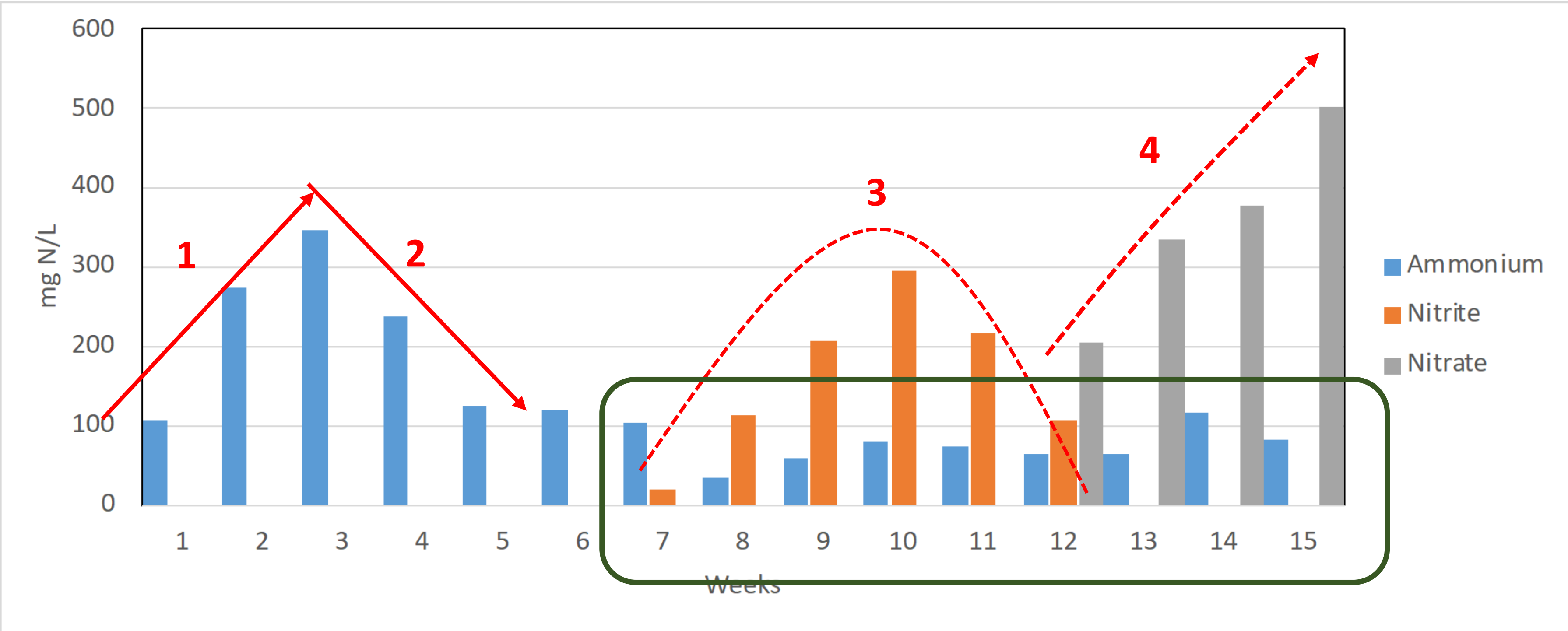


Athens Site (Fili-Ano Liosia MSWTP)

$$SO_4^{2-}(liq) + 2NH_4OH(liq) \rightarrow (NH_4)_2SO_4\,(liq)$$

FIRST RESULTS

CADIZ Site

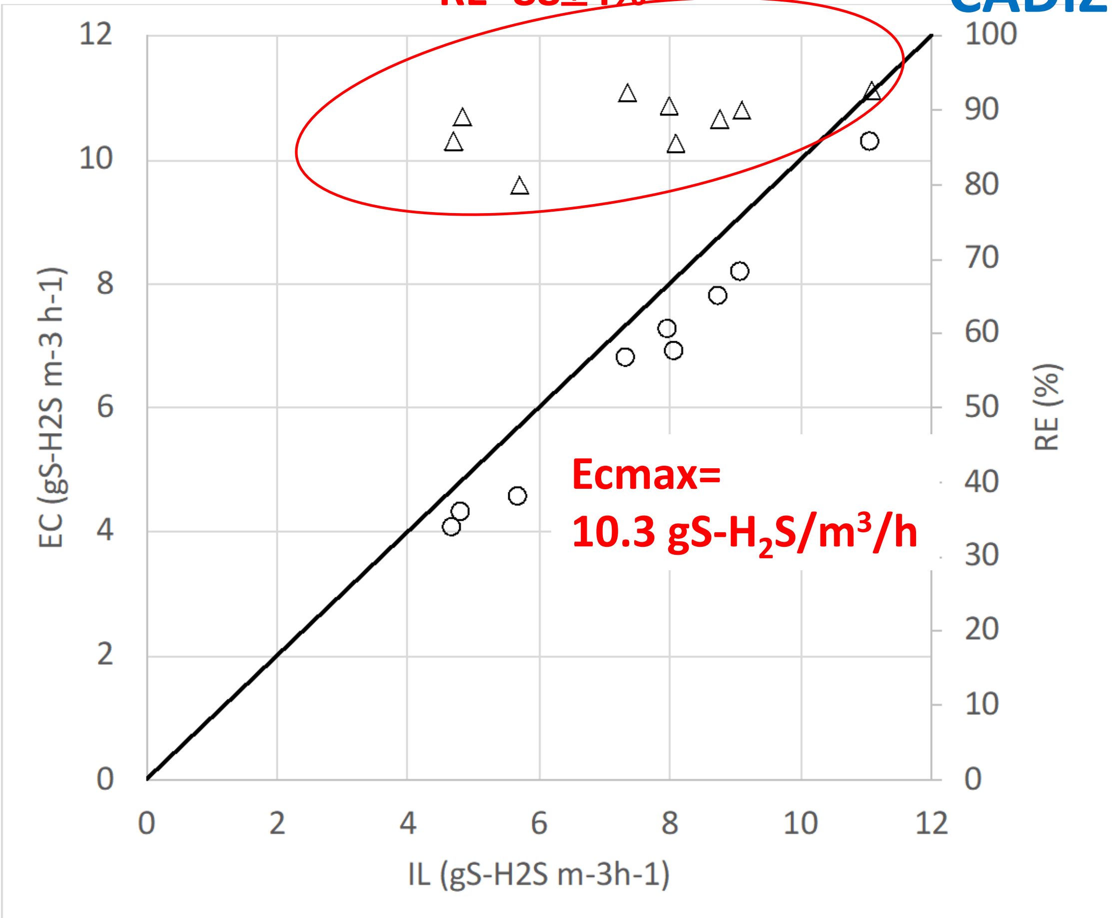


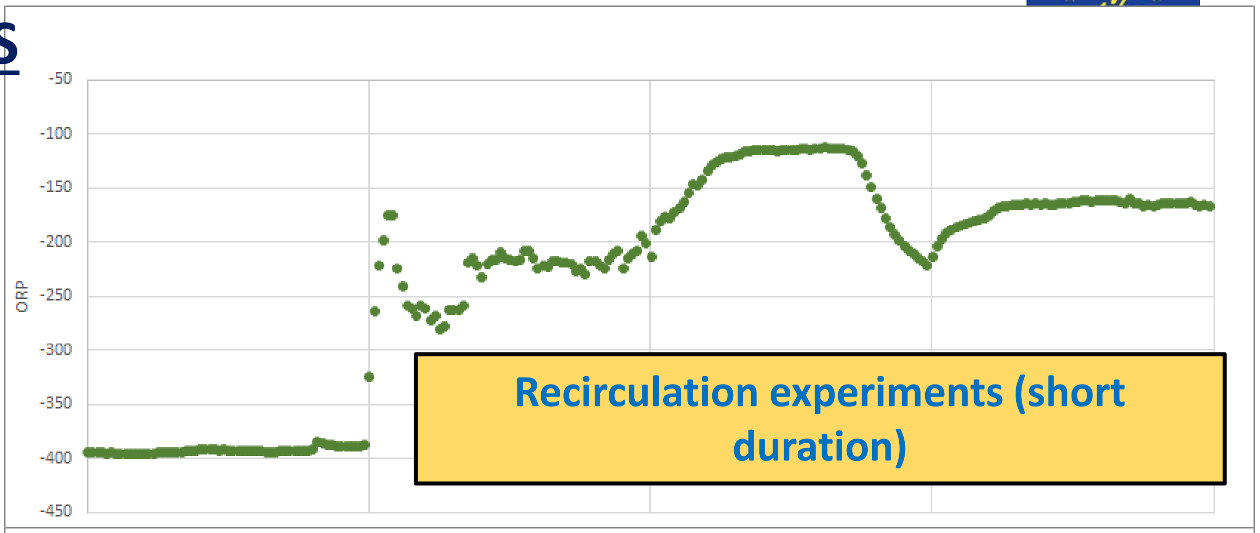
1. NH_4^+ accumulation
2. NH_4^+ consumption
3. Nitrite accumulation
4. NO_3^- accumulation

FIRST RESULTS

CADIZ Site

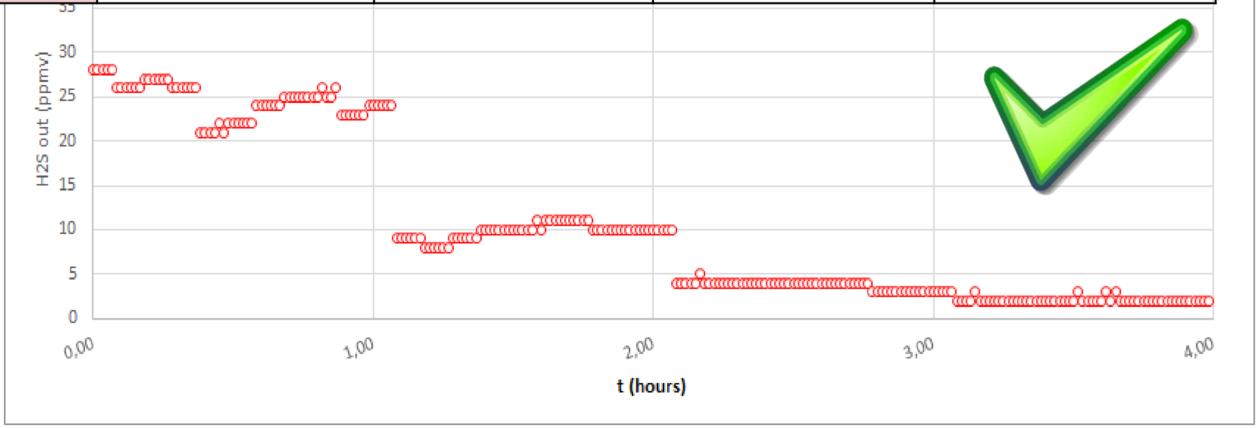
RE=88±4%





Recirculation experiments (short duration)

RE	79,4%	91,9%	96,9%	98,2%



MAIN CONCLUSIONS/TAKE HOME IDEAS

- ✓ Biological technologies can substitute physical-chemical technologies for biogas desulfurization.
- ✓ Aerobic desulfurization in biotrickling filters has some operational drawbacks at high H_2S concentrations
- ✓ Anoxic desulfurization avoids mass transfer limitations and biogas dilution
- ✓ BIOGASNET is a promising technology which couples ammonia/nitrate denitrification and biogas desulfurization

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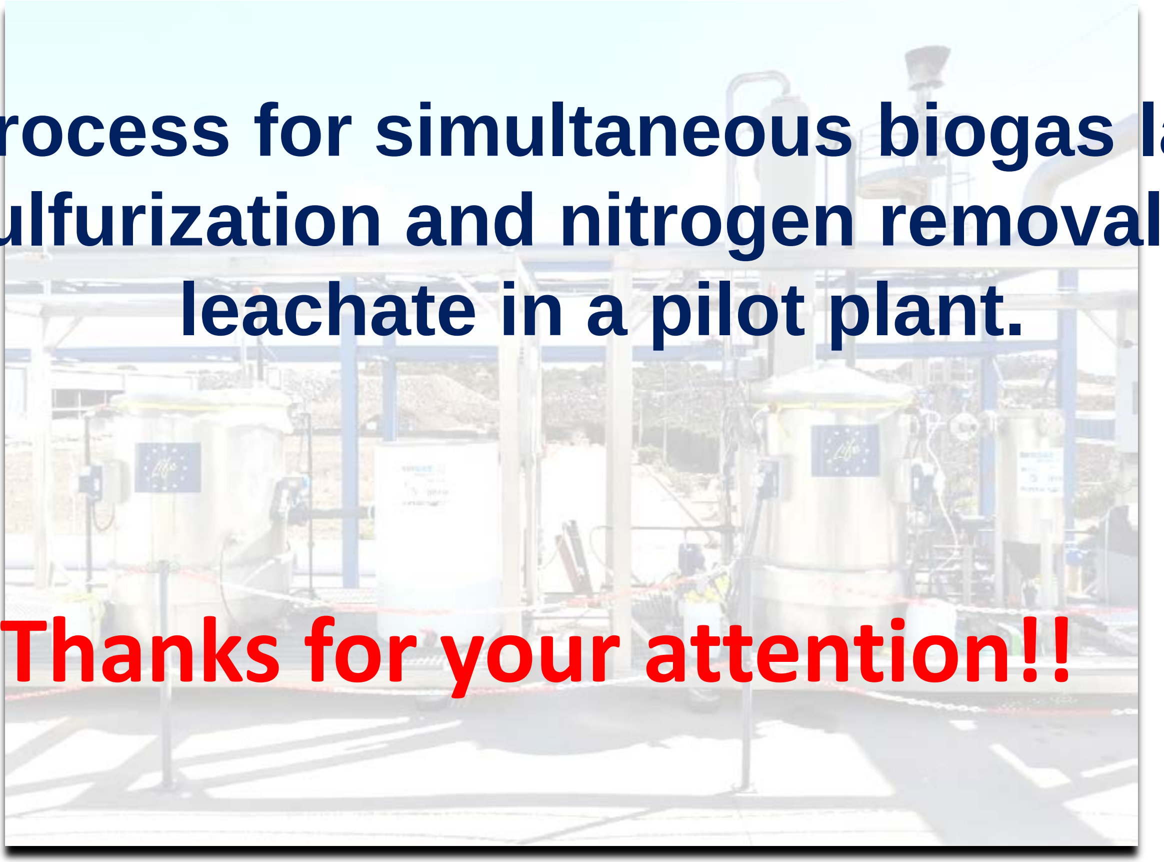

Thanks for your attention!!

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

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