Biofiltración de emisiones gaseosas: fundamentos y aplicaciones

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- Tools that help us in improving knowledge

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- Case study 2: Biogas desulfurization with high performance Biotrickling Filters

Who we are

Valorization and Biological treatment of wastewaters and waste gases: www.genocov.com

Part of the BIOGLS Technological Center (TECNIO)

More than 20 years of experience in biological treatment of wastewater and waste gases

Research Group of biological treatment of gaseous pollutants and odors (TRAGASOL)

Department of Mining, Industrial and ITC Engineering
Universitat Politècnica de Catalunya

www.biofiltration.cat

Aims:

1. Characterization of gaseous emissions
2. Development and characterization of reactors for the biological treatment and valorization of gaseous emissions

Odor and GHG emissions from MSWTP and WWTP

NH_3 emissions from MSWTF

NOx or SOx from combustion processes

Biogas desulfurization

Gaseous emissions

- Very complex
- Odorants and GHG
- Highly variable
- Dis/continuous emissions

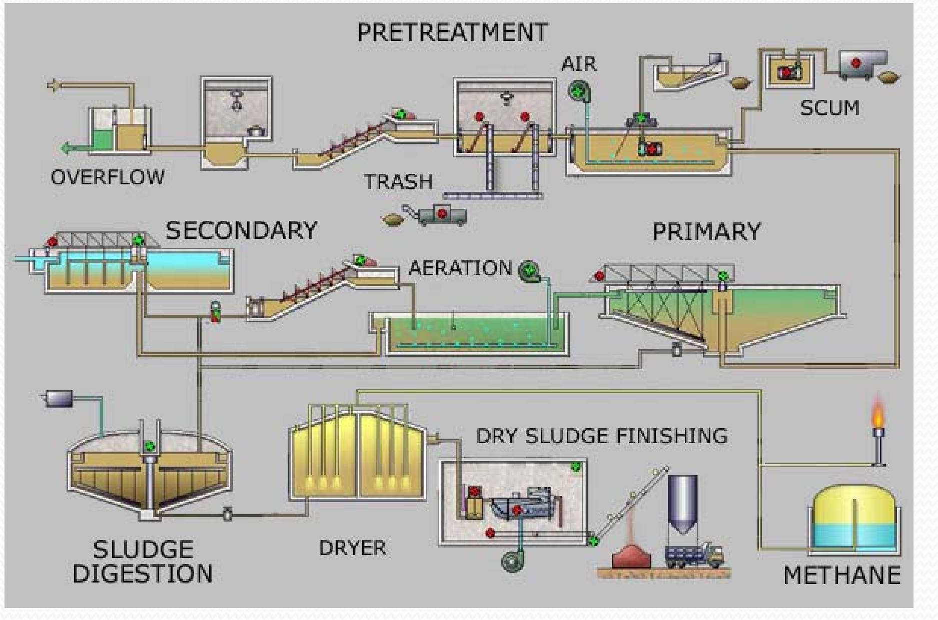
Location	H_2S	RSC	NH_3	VOC-NM	CH_4	N_2O	CO_2
Sewer	high	medium	low	medium	medium	medium	medium
Barscreens	medium	medium	low	medium	low	low	low
Grit chambers	low	medium	low	medium	low	low	low
Primary	medium	medium	low	medium	low	low	low
Activ. Sludge	low	low	low	low	low	medium	medium
Thickeners	high	medium	medium	medium	low	low	low
AD (biogas)	high	low	low	low	high	low	high
Dewatering	high	medium	medium	high	medium	low	medium

Impact (no treatment): high medium low

Example: WWTP

Gaseous emissions

- Very complex
- Odorants and GHG
- Highly variable
- Dis/continuous emissions
- Depend largerly on plant configuration and operational practices
- Large social concern
- Lack of regulation of odor emissions



Gaseous emissions

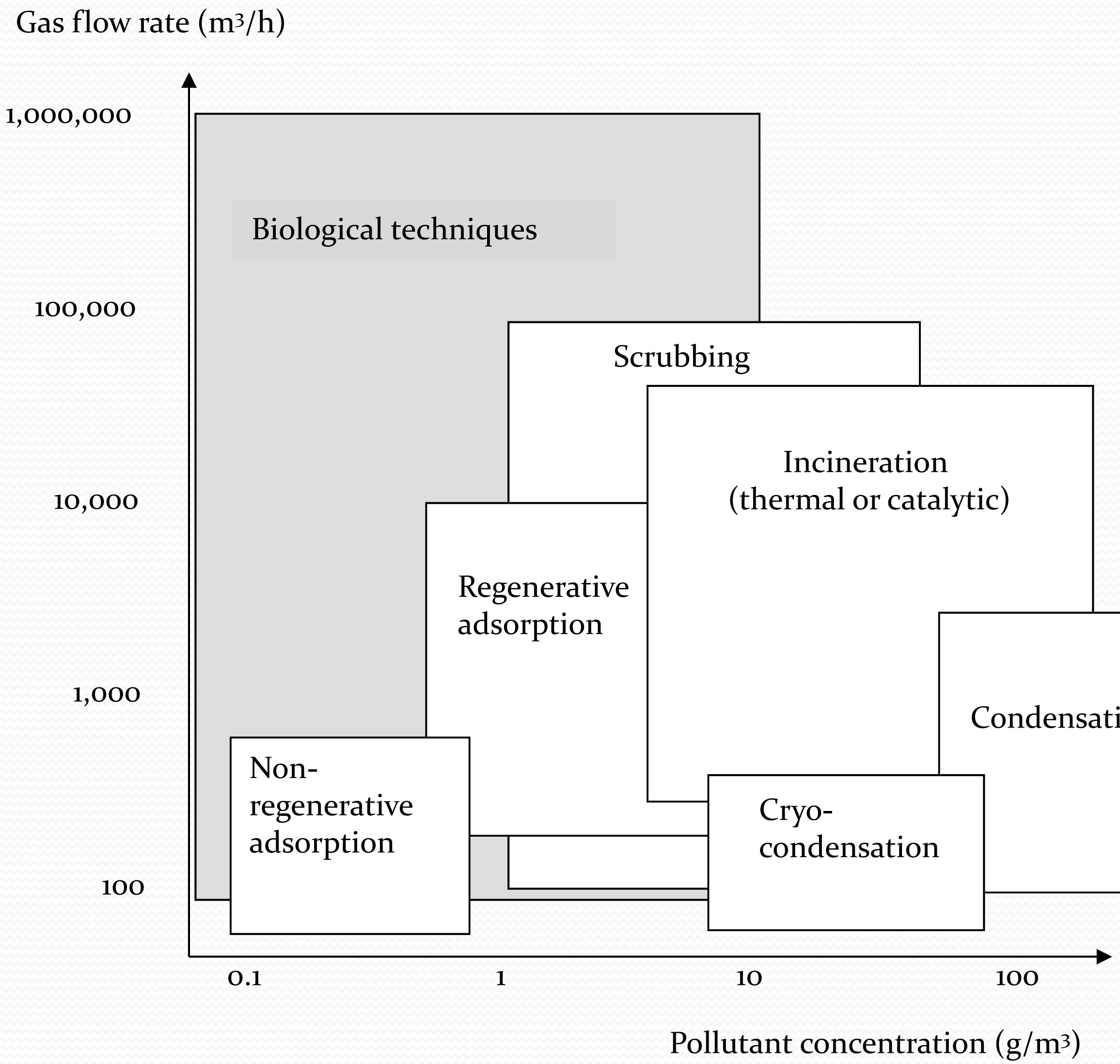
- Very complex
- Odorants and GHG
- Highly variable
- Dis/continuous emissions
- Depend largerly on plant configuration and operational practices
- Large social concern
- Lack of regulation of odor emissions

We need to characterize and treat emissions to avoid nuisance and other impacts

Characterization of gaseous emissions

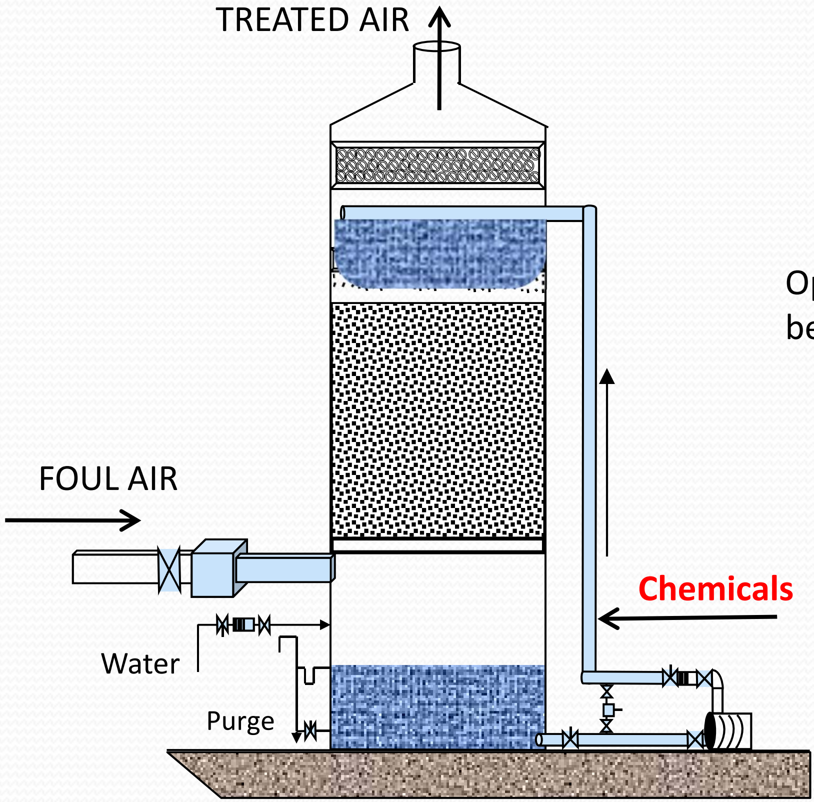
Target?

Available technologies

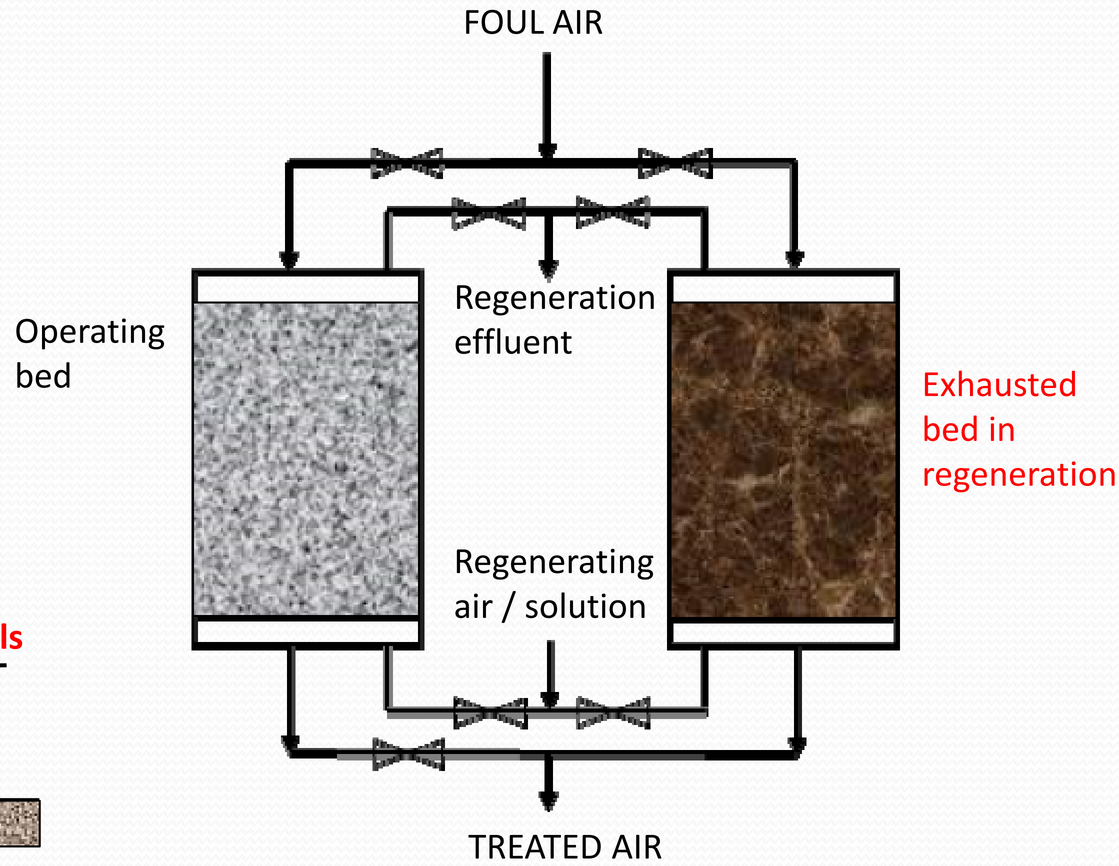


Physical-chemical techniques

SCRUBBER



ADSORBER

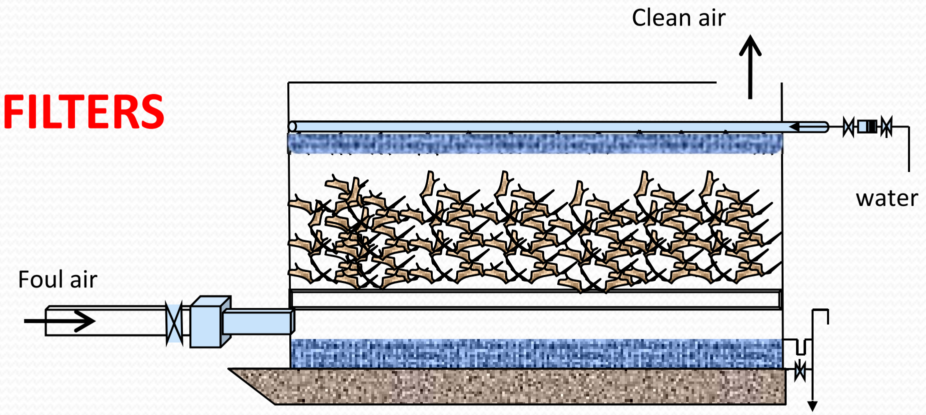


Physical-chemical techniques

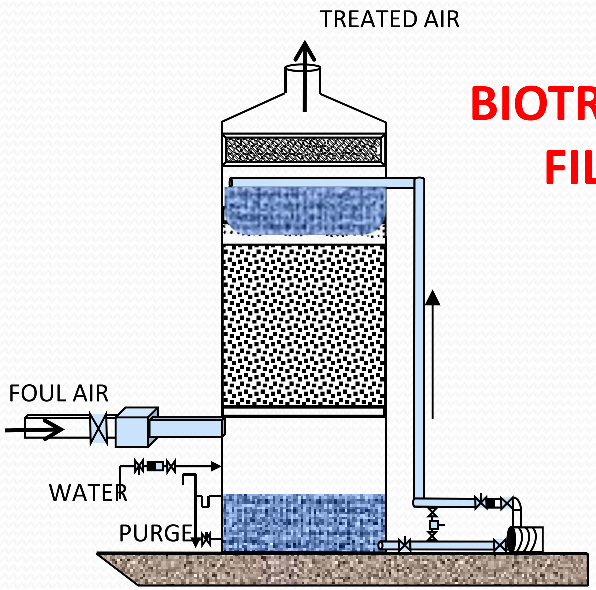
- Well-established at industrial scale
- Proven reliable, stable, robust and effective for H_2S and NH_3 (scrubbers) and VOCs (adsorbers)
- Fast startup
- Large operating costs for diluted gas flows
- Chemicals usage or bed replacement/regeneration

Mature biological techniques

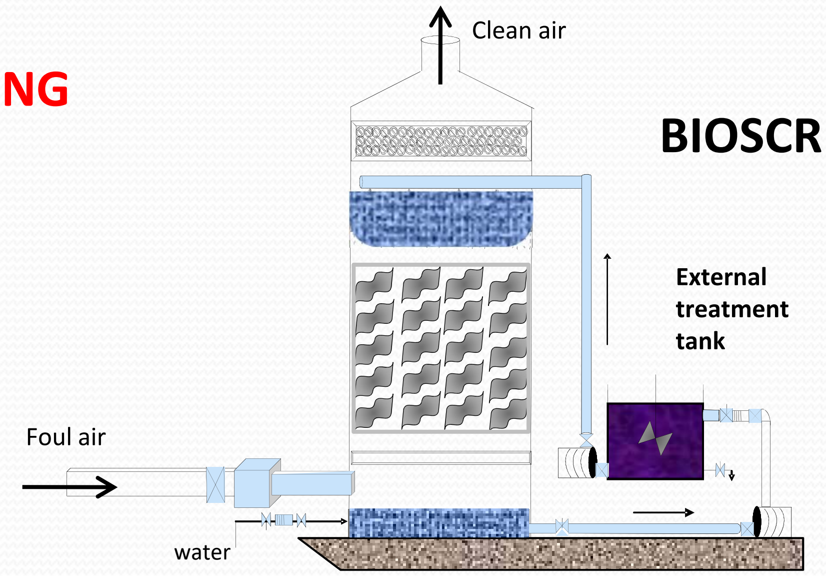
BIOFILTERS



BIOTRICKLING FILTERS



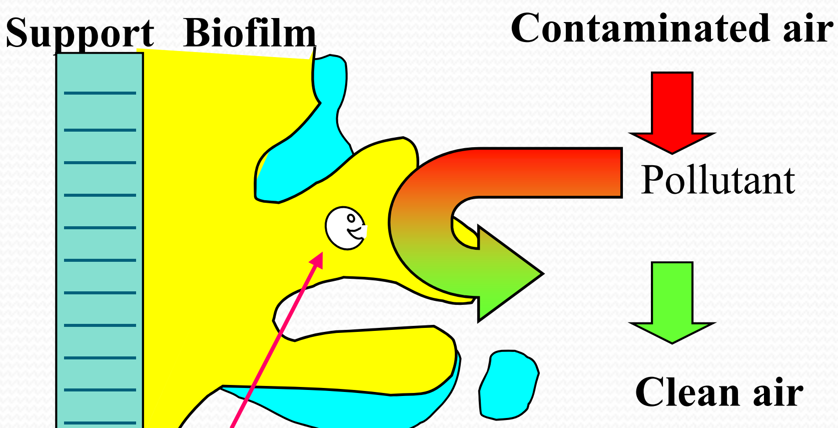
BIOSCRUBBERS

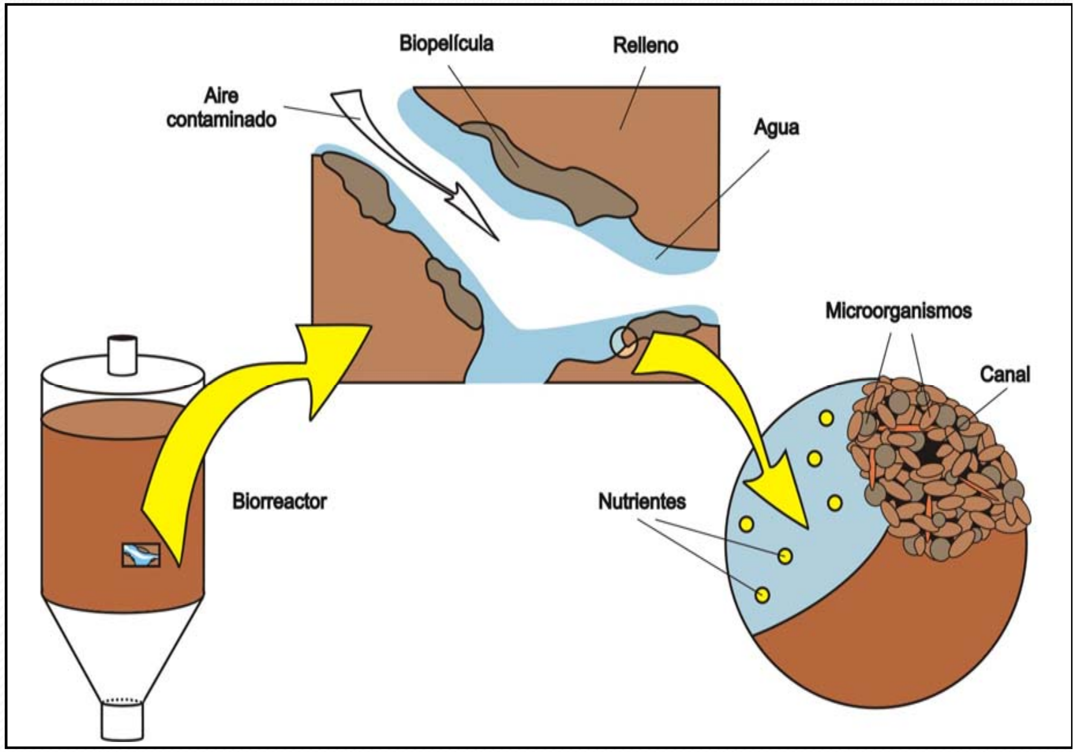


(most popular)

Packed bed type reactors: microorganisms grow as a biofilm

Pollutant +  + O_2 ⇨ $CO_2 + H_2O$ + biomass





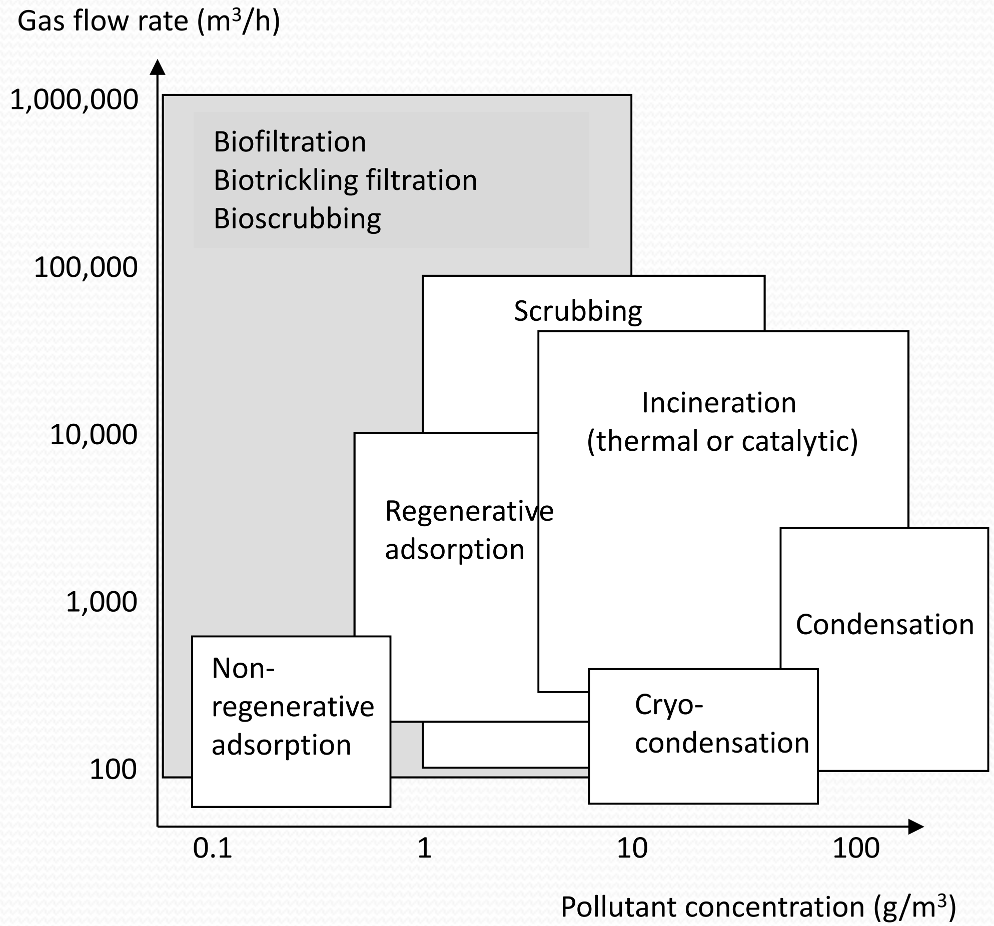
Multiphase bioreactors mean multiple potential limiting steps

A simple open bed biofilter system

Large biotrickling filters for odor control

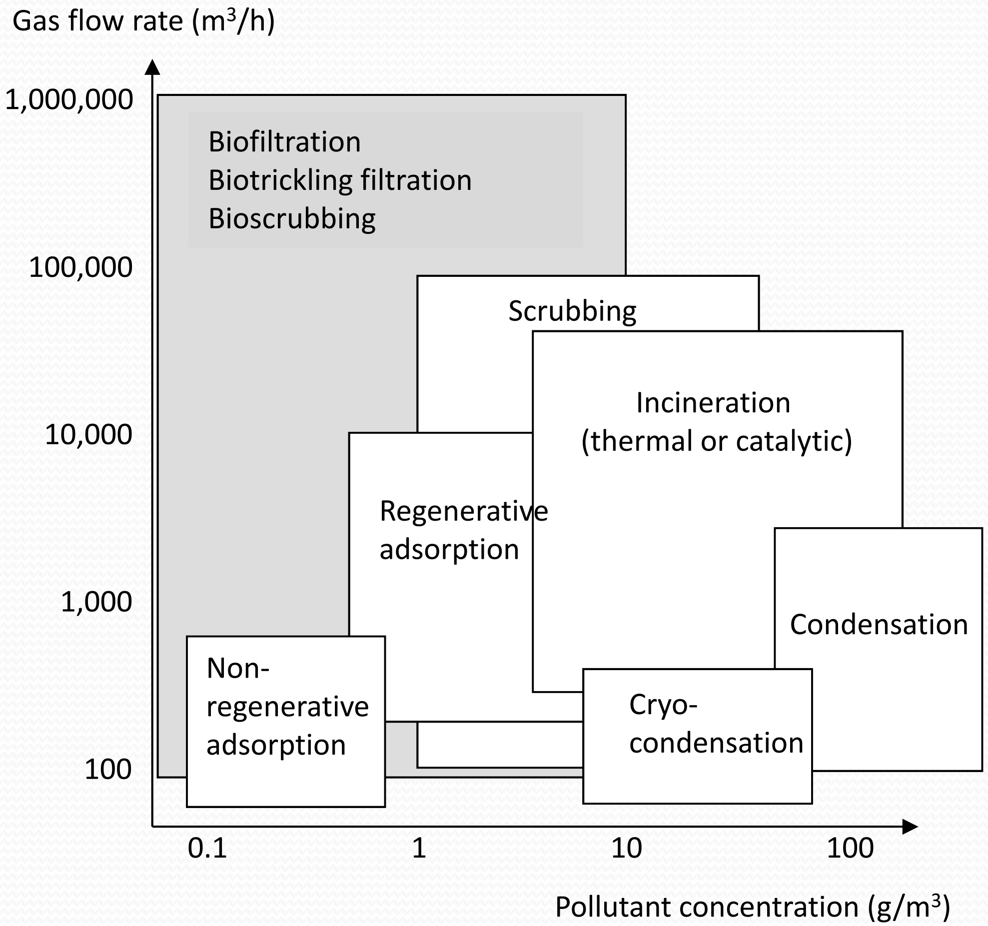
Advantages and drawbacks

- No chemicals: Reduced risks
- Reduced operating costs
- Effective for large gas flowrates with low concentrations of pollutants
- True pollutant degradation
- Proven reliable and robust at full-scale



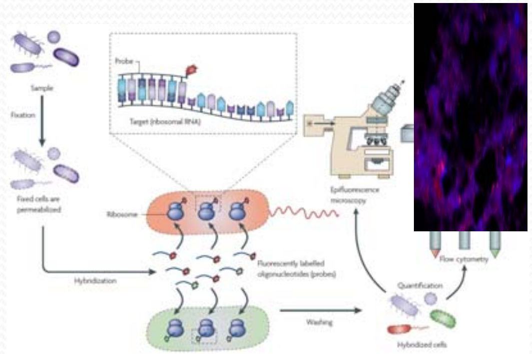
Advantages and drawbacks

- Treats only biodegradable and soluble compounds
- Needs cooling of air to reasonable temperatures
- Startup time can be long
- Clogging risks at medium/high loads
- Discontinous emissions may negatively affect process performance
- Needs some understanding of microbiology

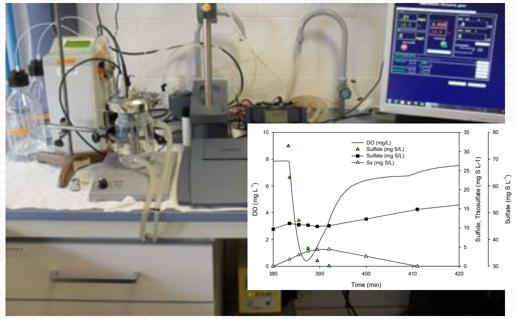


Tools that help us in improving knowledge

- Molecular biology tools for assessing microbial diversity and its evolution along time

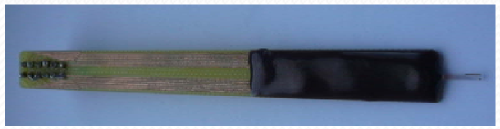


- Respirometry and titrimetry to determine degradation mechanisms as well as kinetic and stoichiometric parameters

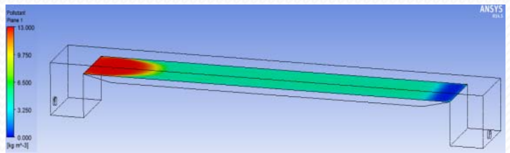


- Intensive contactors and vectors for gas-liquid mass transfer improvement

- Microelectrodes for assessing concentrations inside biofilms

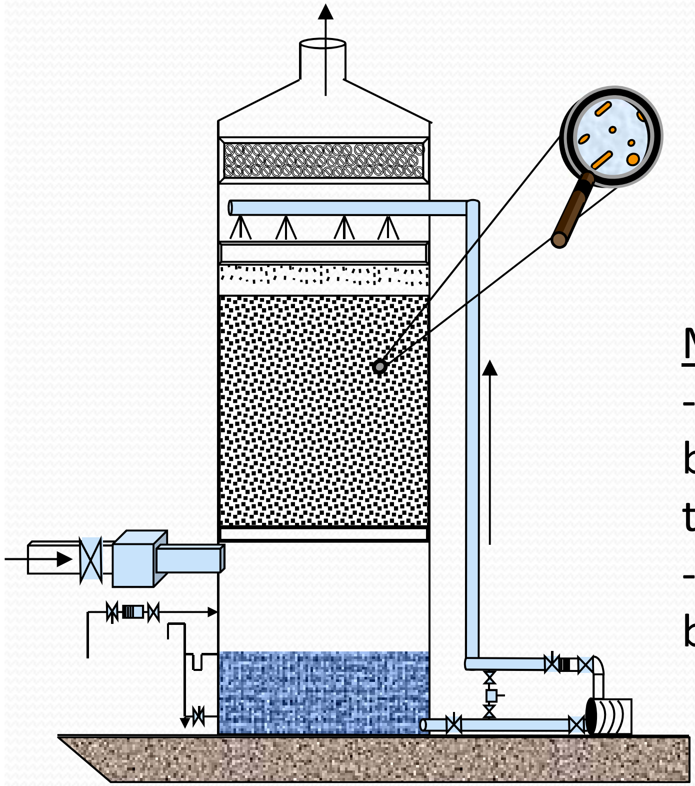


- Modelling tools for… everything!



Molecular biology tools for assessing microbial diversity and its evolution along time

The optimization and improvement in the design and operation of bioreactors needs of a deep study and characterization of the biocatalysts



Which are the relevant microorganisms?

How populations evolve along time?

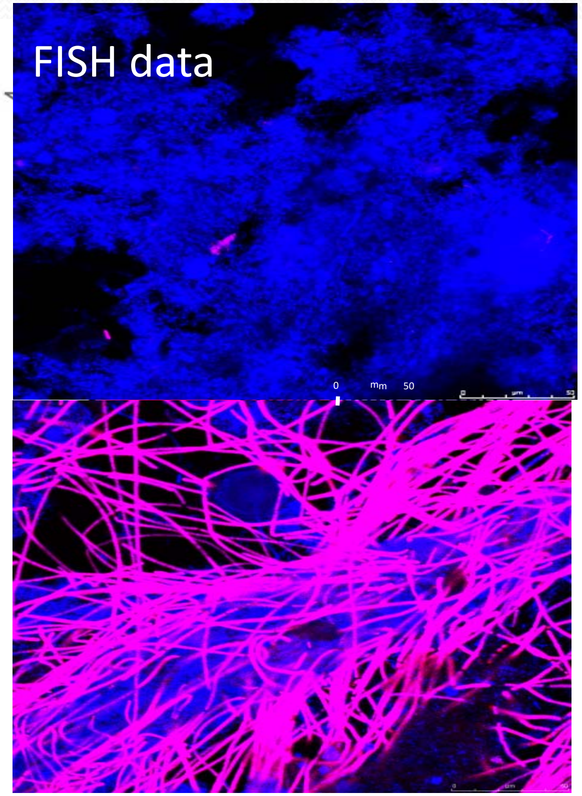
How operating conditions affect the microbial ecology?

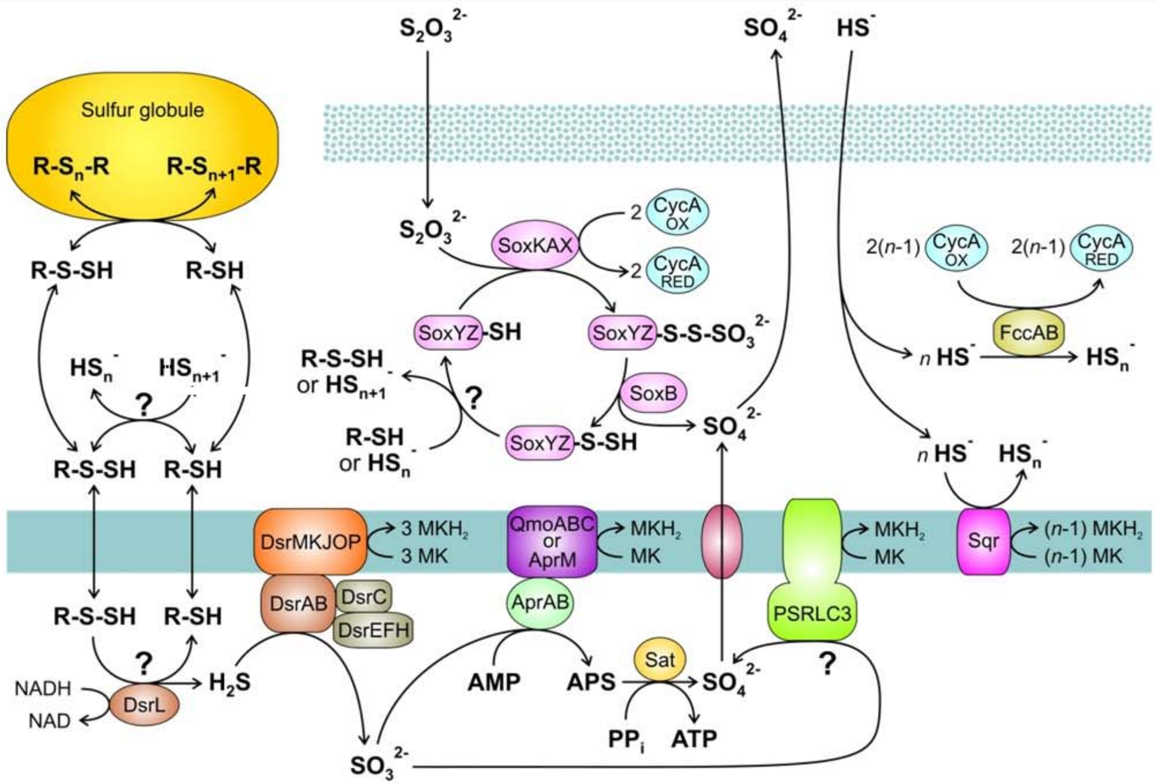
Which are the removal mechanisms involved?

Main goals:

- To gain knowledge by characterizing and understanding basic phenomena during bioreactor operation in relation to the microbial communities
- To improve our capacity to prevent, diagnose and monitor bioreactor performance

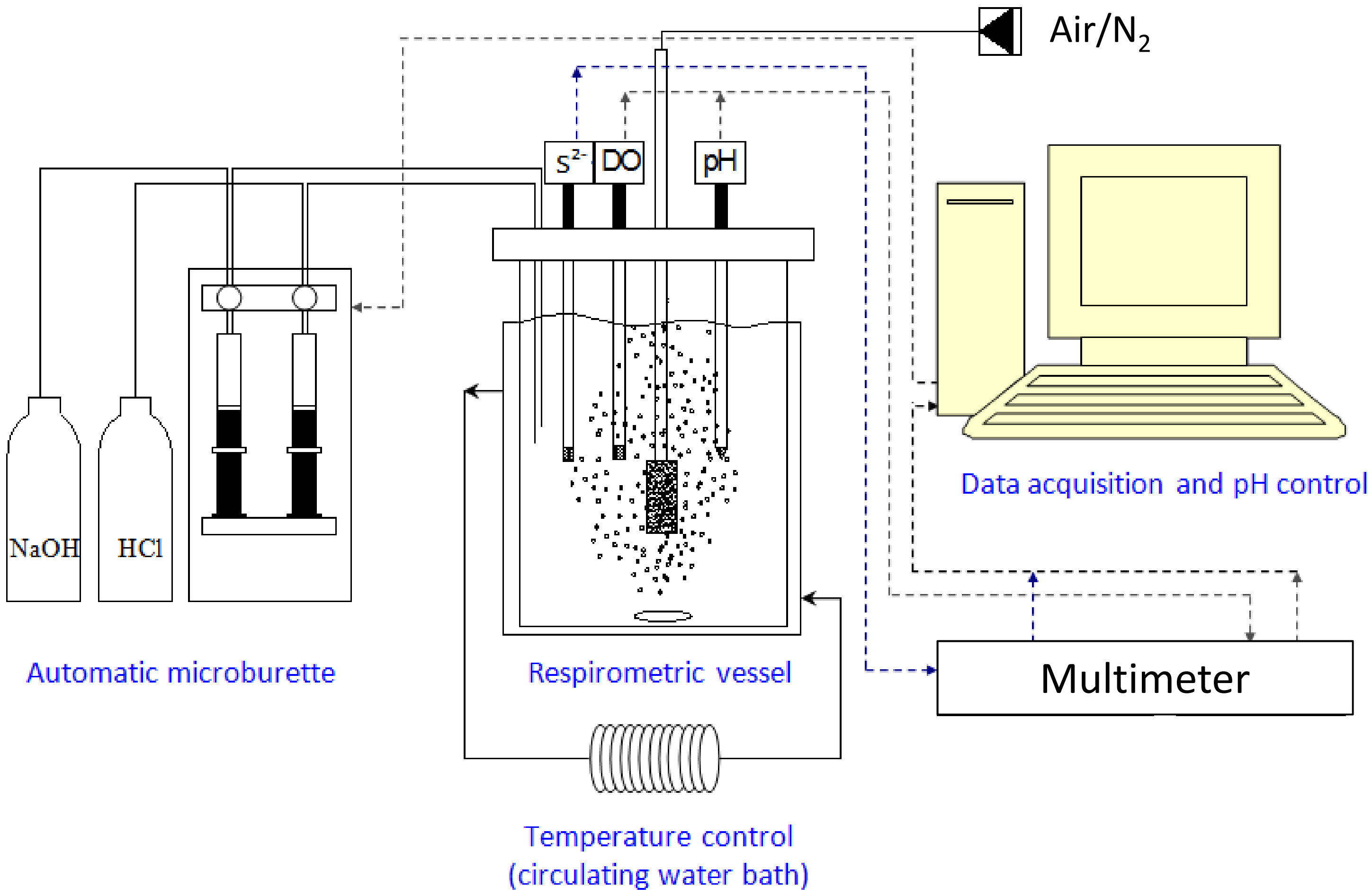
Pyrosequencing and FISH (RNA-based technology) to identify microbial diversity and its evolution along bioreactor operation



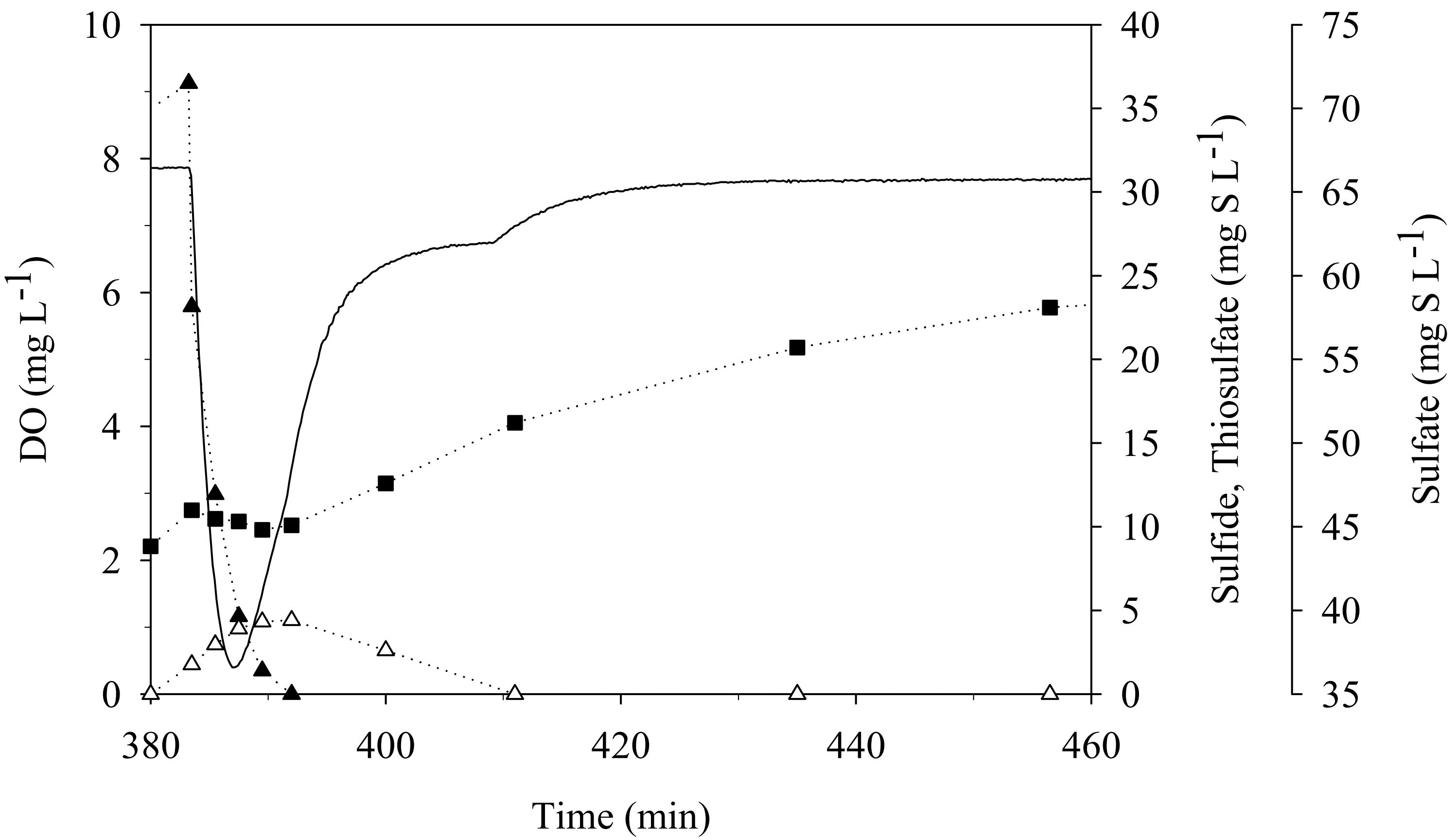


Removal mechanisms, stoichiometry and kinetics depends strongly on microbial community characteristics, and must be determined ad-hoc

Respirometry and titrimetry to determine degradation mechanisms and kinetic and stoichiometric parameters



Respirometry and titrimetry to determine degradation mechanisms and kinetic and stoichiometric parameters

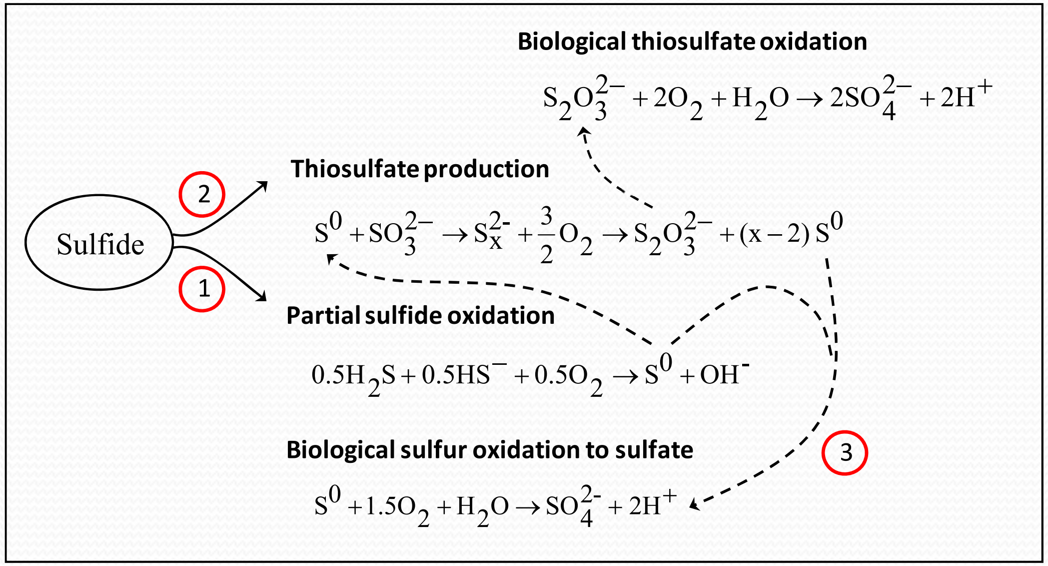


Respirometry and titrimetry to determine degradation mechanisms and kinetic and stoichiometric parameters

- From the information collected…

MECHANISMS

STOICHIOMETRY



Mora et al. Water Research

R. 1: $0.5\ H_2S + 0.5\ HS^- + 0.42\ O_2 + 0.075\ CO_2 + 0.005\ HCO_3^- + 0.016\ NH_4^+ + 0.489\ H^+ \rightarrow$

$\mathbf{0.016\ C_5H_7NO_2} + \mathbf{S^0} + 0.973\ H_2O$

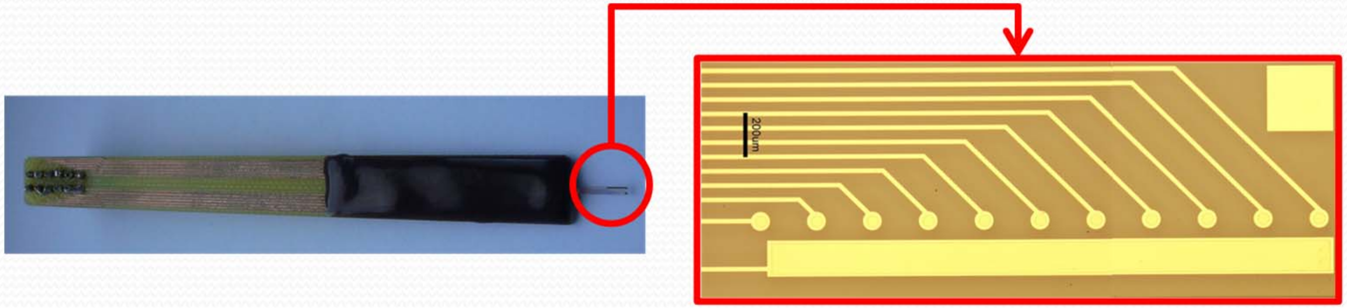
R. 2: $S^0 + 1.22\ O_2 + 0.267\ CO_2 + 0.018\ HCO_3^- + 0.057\ NH_4^+ + 1.10\ H_2O \rightarrow$

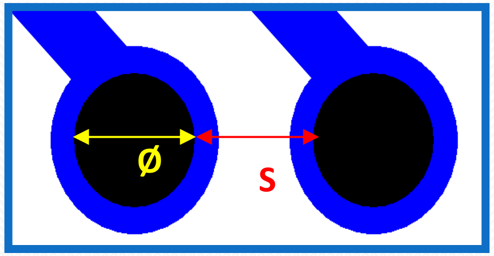
$\mathbf{0.057\ C_5H_7NO_2} + \mathbf{SO_4^{2-}} + 2.04\ H^+$

Microelectrodes for assessing concentrations inside biofilms

Development of a **Multi-Analite microsensor**, based on MEMS technology, for the measurement of:

- ✓ **Chemical species**
- ✓ **Mass transport properties**





Ø=S=50µm

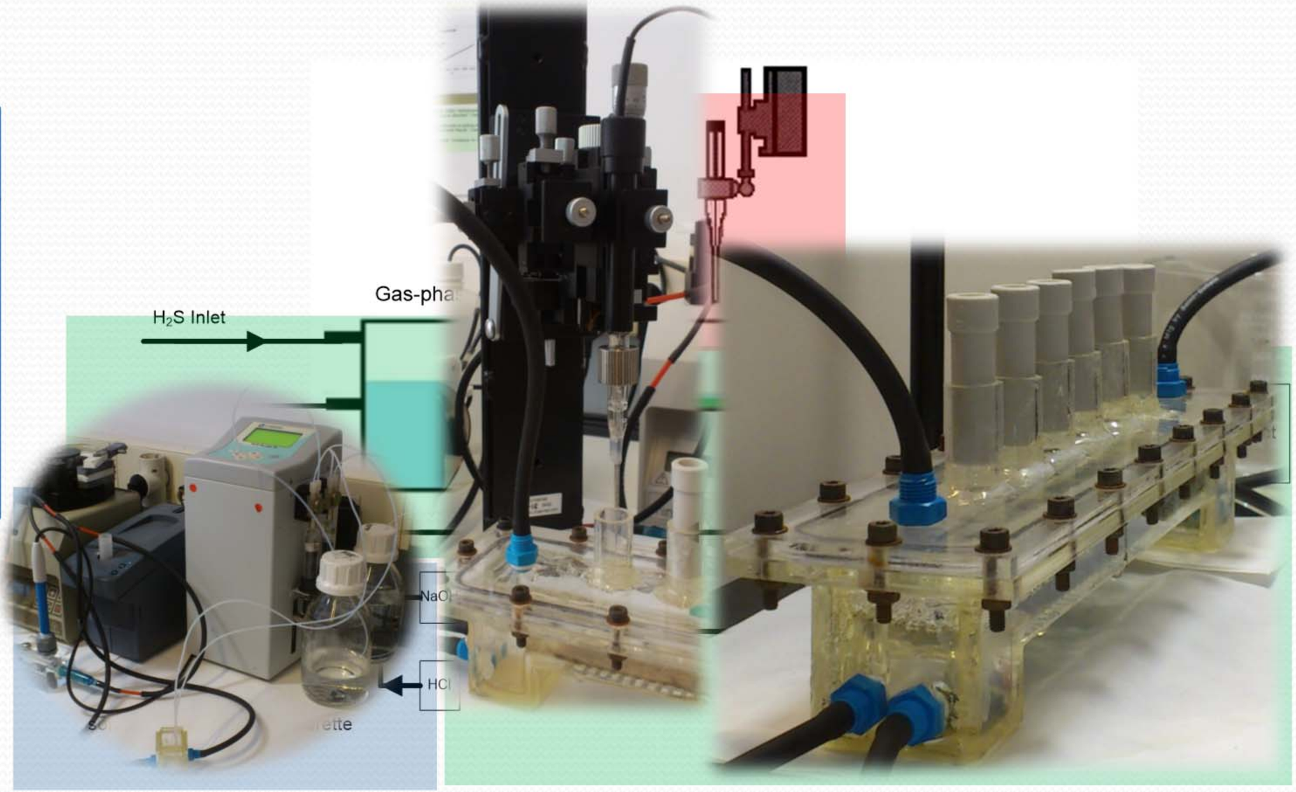
11 gold electrodes of 50µm diameter designed as working electrodes. 1 macroelectrode of 0.115 cm^2 designed as reference electrode

Novel alternative: Inkjet printing

Microelectrodes for assessing concentrations inside biofilms

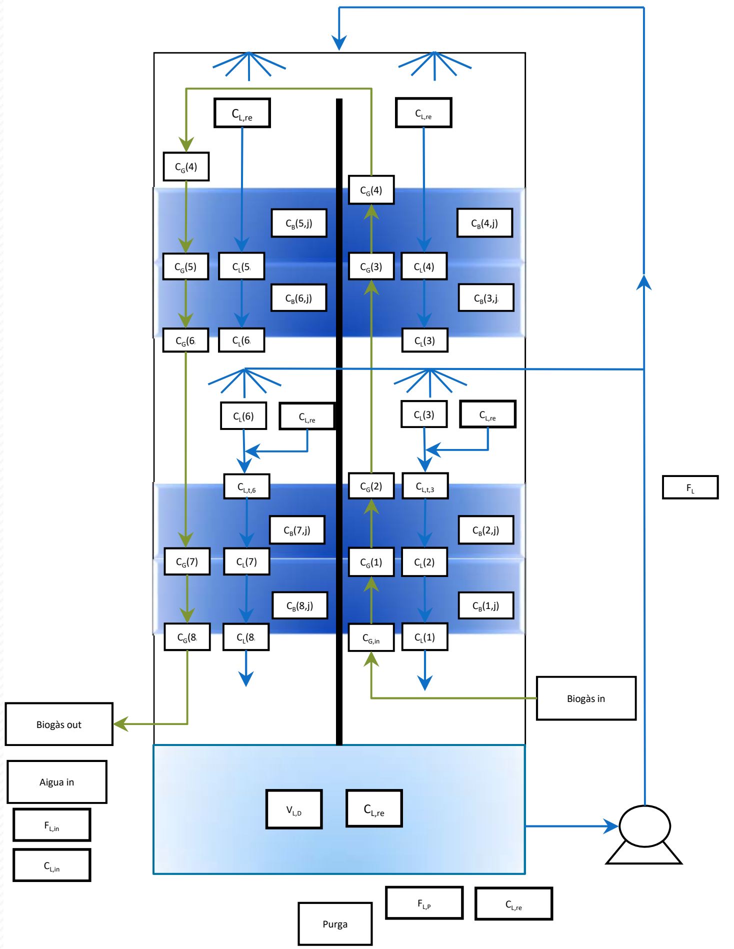
- Biofilm growth → Dynamic characteristics monitoring
- Lab-scale biofilm reactor (Flat Plate Bioreactor), reproducing the operation conditions of a biofilm-based reactor

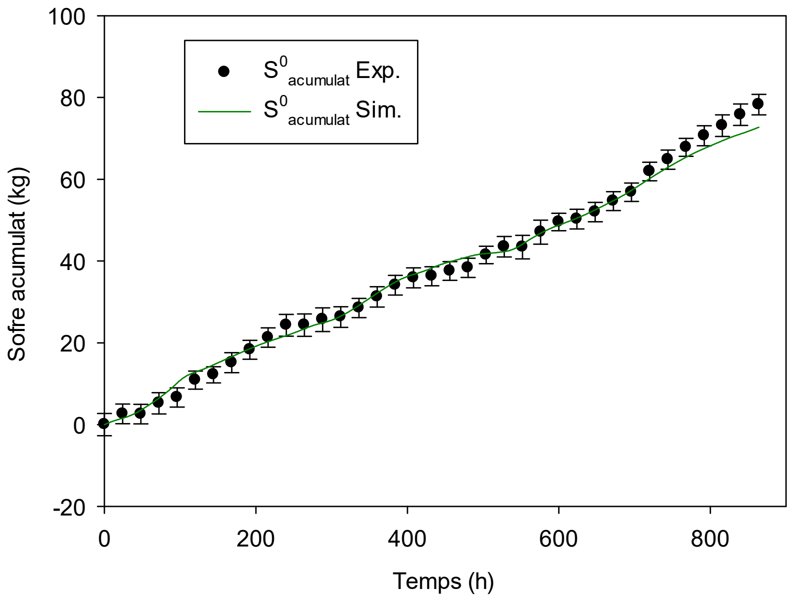
MAIN DESIGN FACTORS
Type of reactor
Biological process control
Biofilm measurements



Advanced modelling tools

From rigorous models built in a home-made software environment…



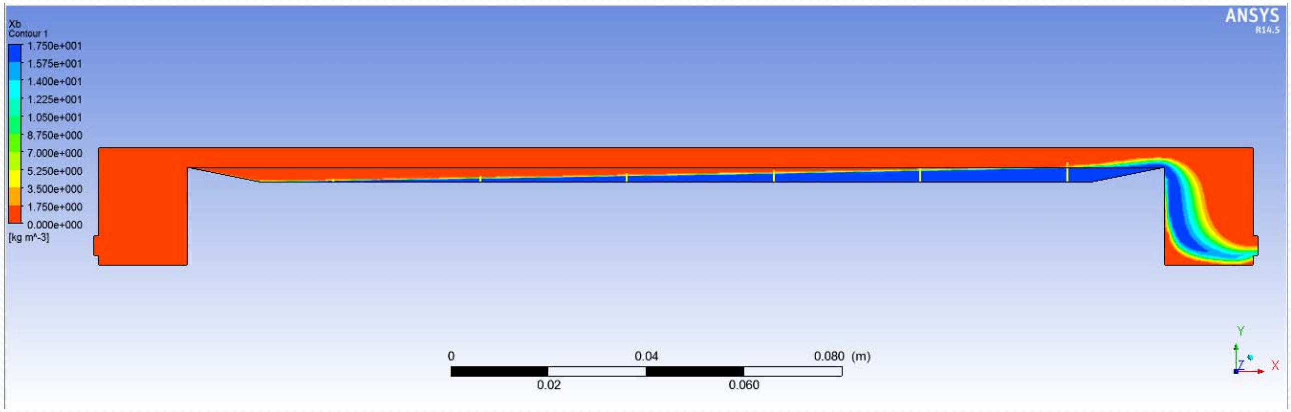


Elemental sulfur accumulation predicted in an industrial BTF for biogas desulfurization

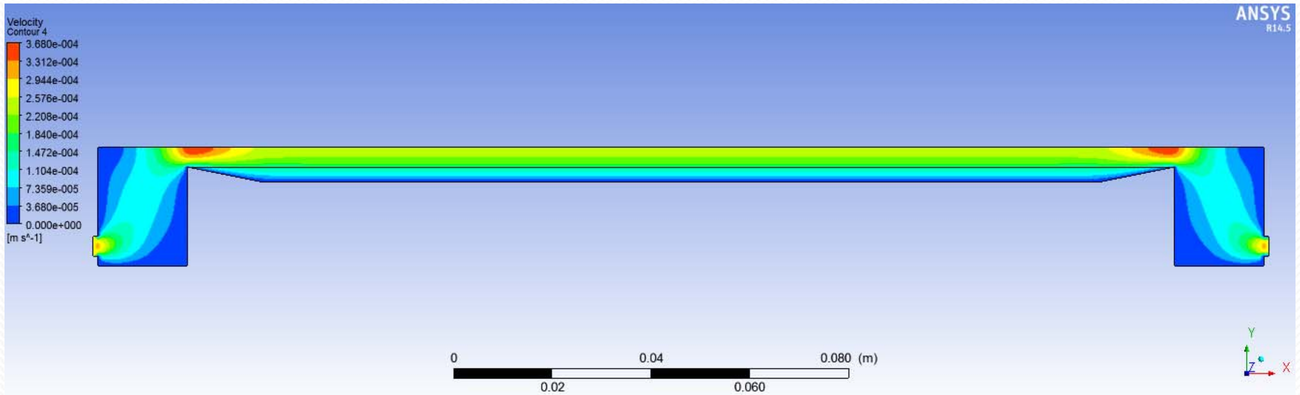
Advanced modelling tools

Modeling of a two-phase Flat Plate Bioreactor: Biomass concentration and velocity profiles

Biomass profile

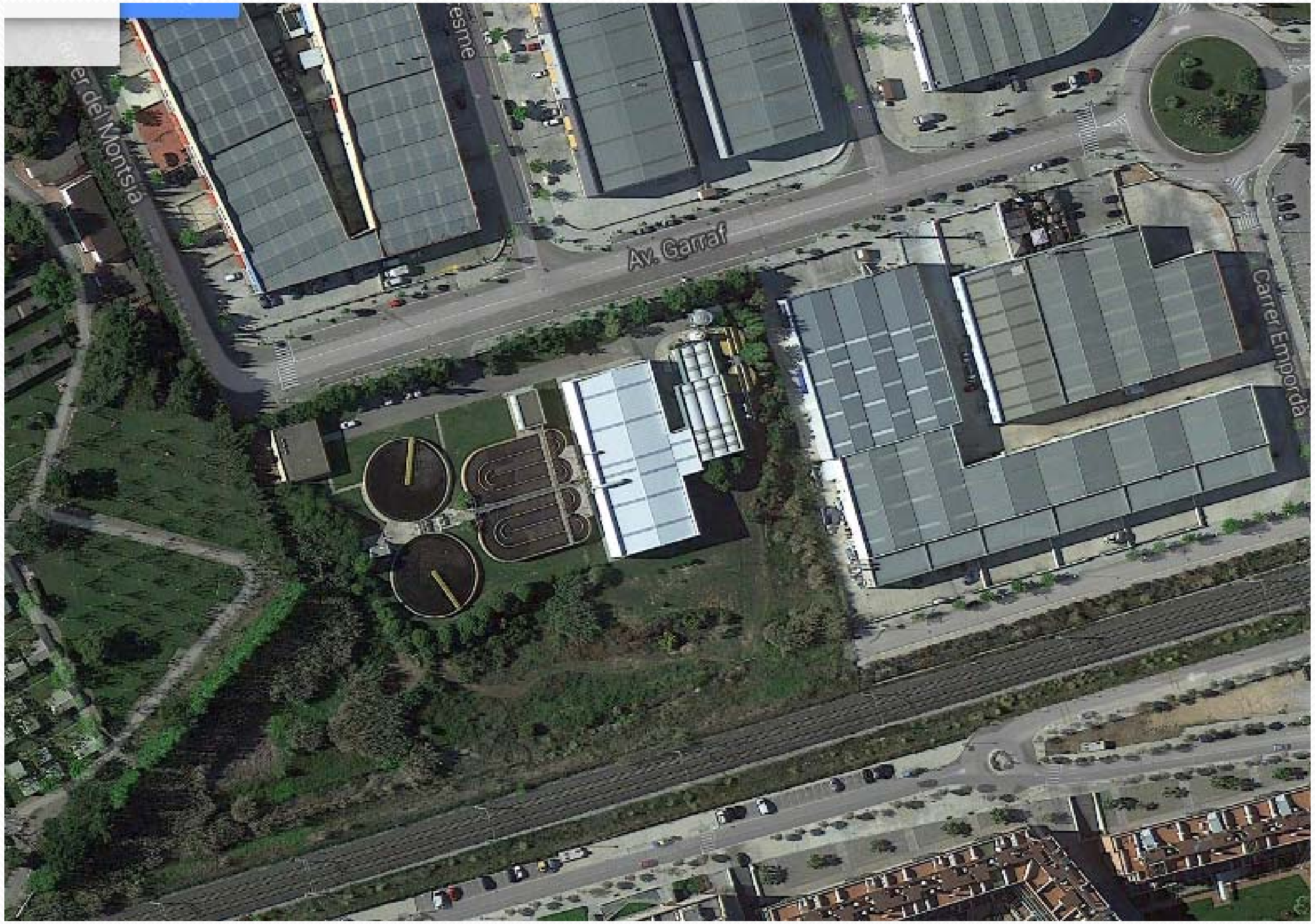


Velocity profile



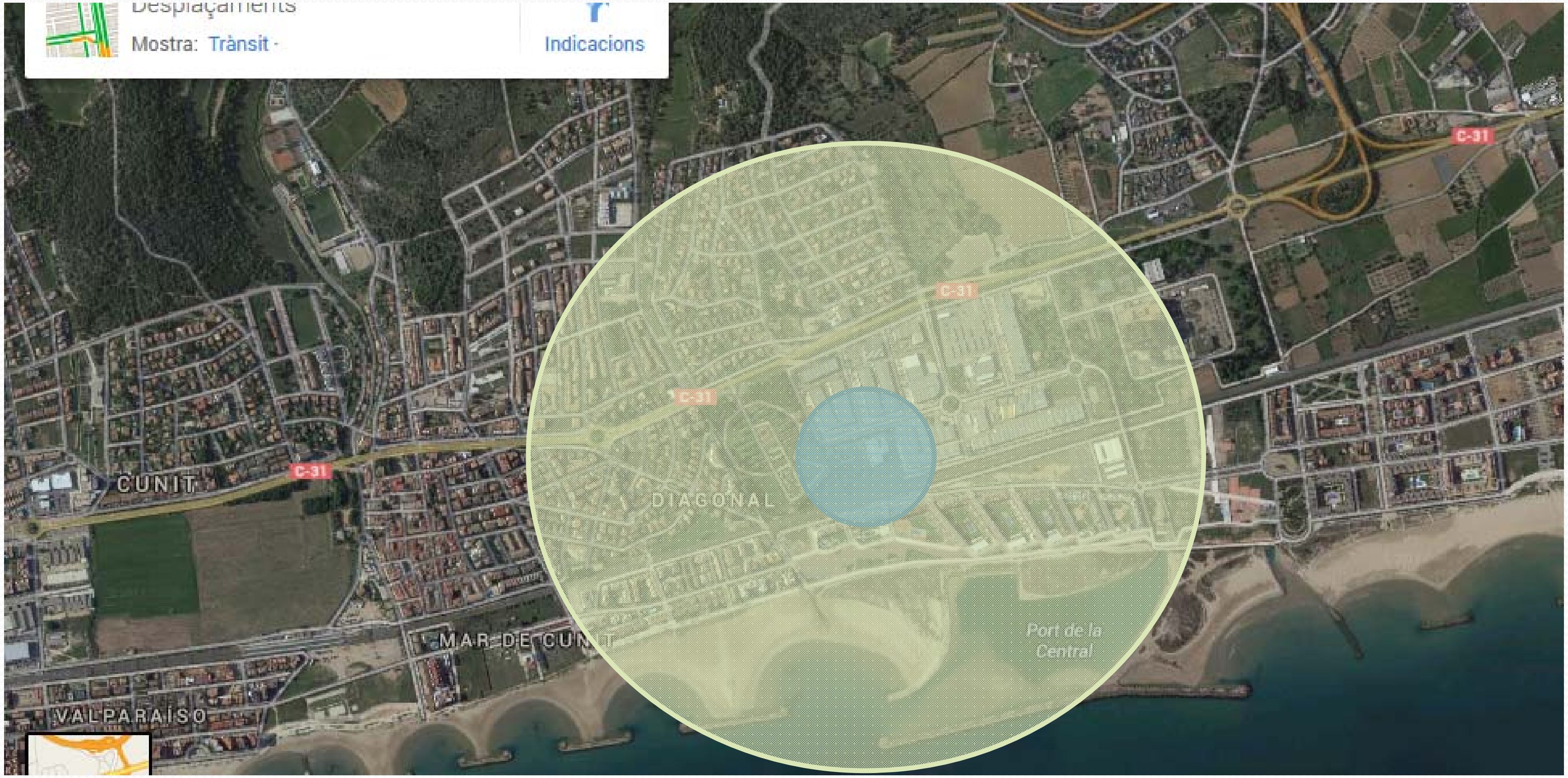
CASE STUDY 1
Biological treatment of odour emissions in a WWTP

Cunit and Cubelles in the Mediterranean Coast



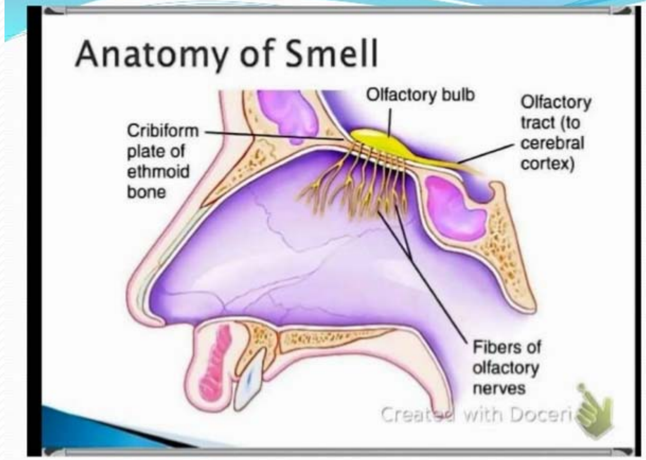
The WWTP is in the middle of a commercial area, and close to residential areas...

Odour affectation to the surroundings is quite likely



Odor is defined as a sensation resulting from the stimulation of sensory cells in the smell due to the presence of gas-phase organic and inorganic chemical compounds.

Olfactory threshold very low for several compounds



Some odor characteristics:

- **Similar substances have very different smells**

  ethylmercaptan (CH_3CH_2SH: rotten cabbage) alylmercaptan (CH_2CHCH_2SH: garlic)

- **Smell may become saturaded rapidly with some substances**

  H_2S → Olfactory detection limit: ~ 0.0047 ppb_v (~6 µg/m^3); saturation 30 - 40 ppm_v

- **Odors are not additive: two or more odors can mask each other**

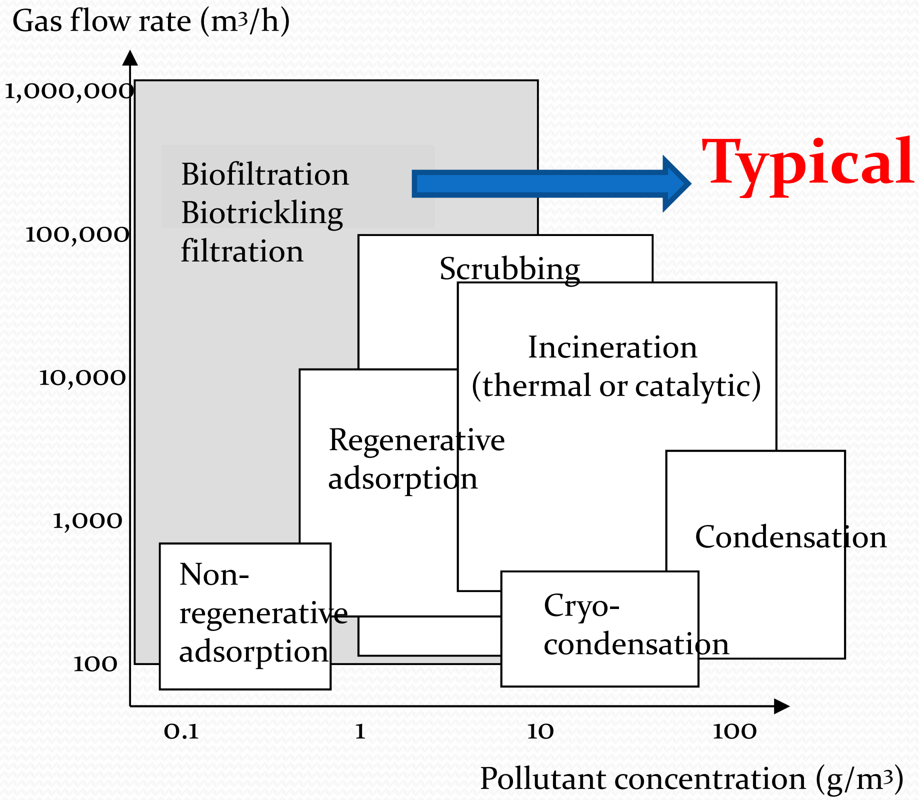
Odour in WWTP are usually treated with conventional physical-chemical technologies:

- 3 Chemical scrubbers in series
  (1 acid, 2 NaOH + NaOCl)
- Main Pollutants; H_2S, VOCs
- Low inlet concentrations
  H_2S inlet = 1 – 40 ppm_v
  COVs inlet = 0 – 6 ppm_v

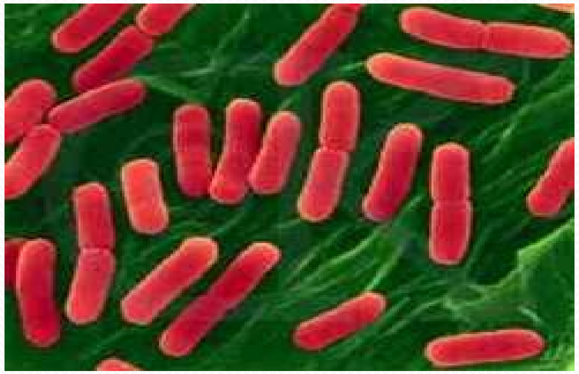
The challenge: to substitute reagents consumption by bacteria, with minimum investment and/or modification of the actual configuration

Pollutant + microorganisms + O_2 → Harmless end-products

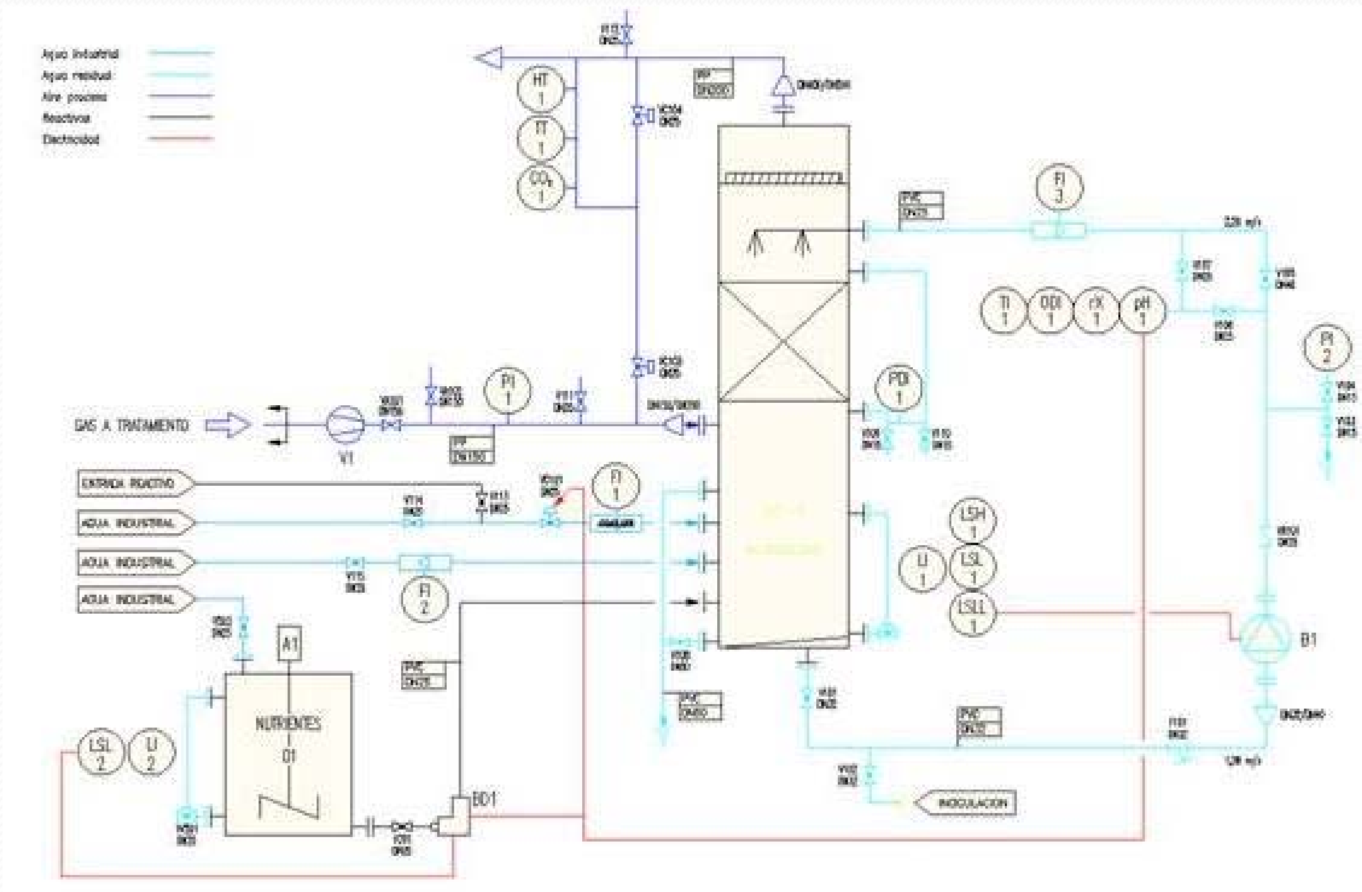
- **Main problem: Contact time (EBRT)**



Typical EBRT values: 30-90 s

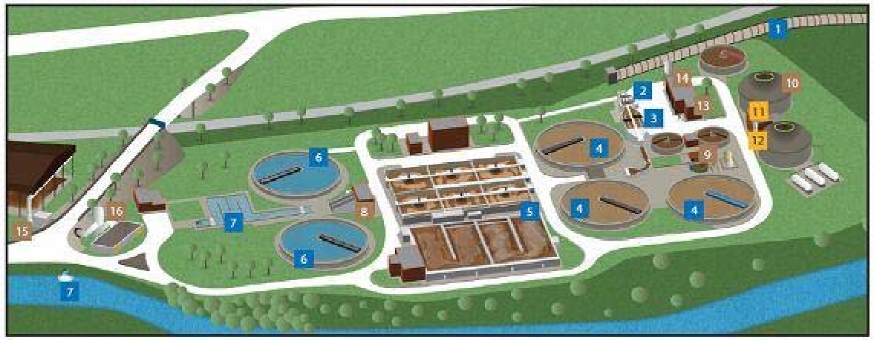


Pilot plant (BTF) designed *ad hoc* to test how much "stress" can overcome our bacteria



Construction and installation of a pilot plant (WWTP Manresa)

Before pilot plant installation



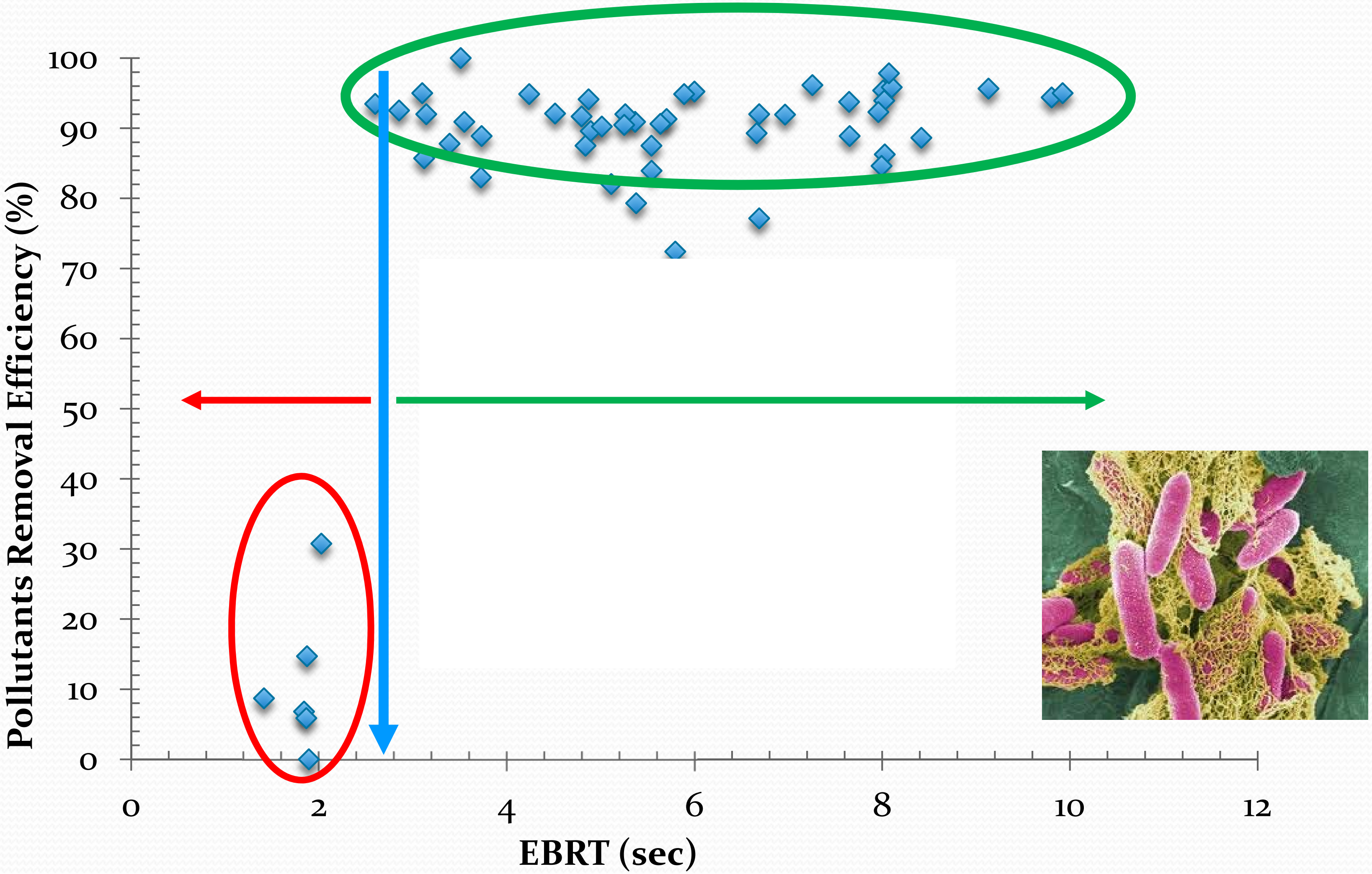
Location of the` pilot plant in the WWTP (16)

AIGÜES DE MANRESA S.A.
empresa municipal

Plant installation

Pilot plant operated during 1 year

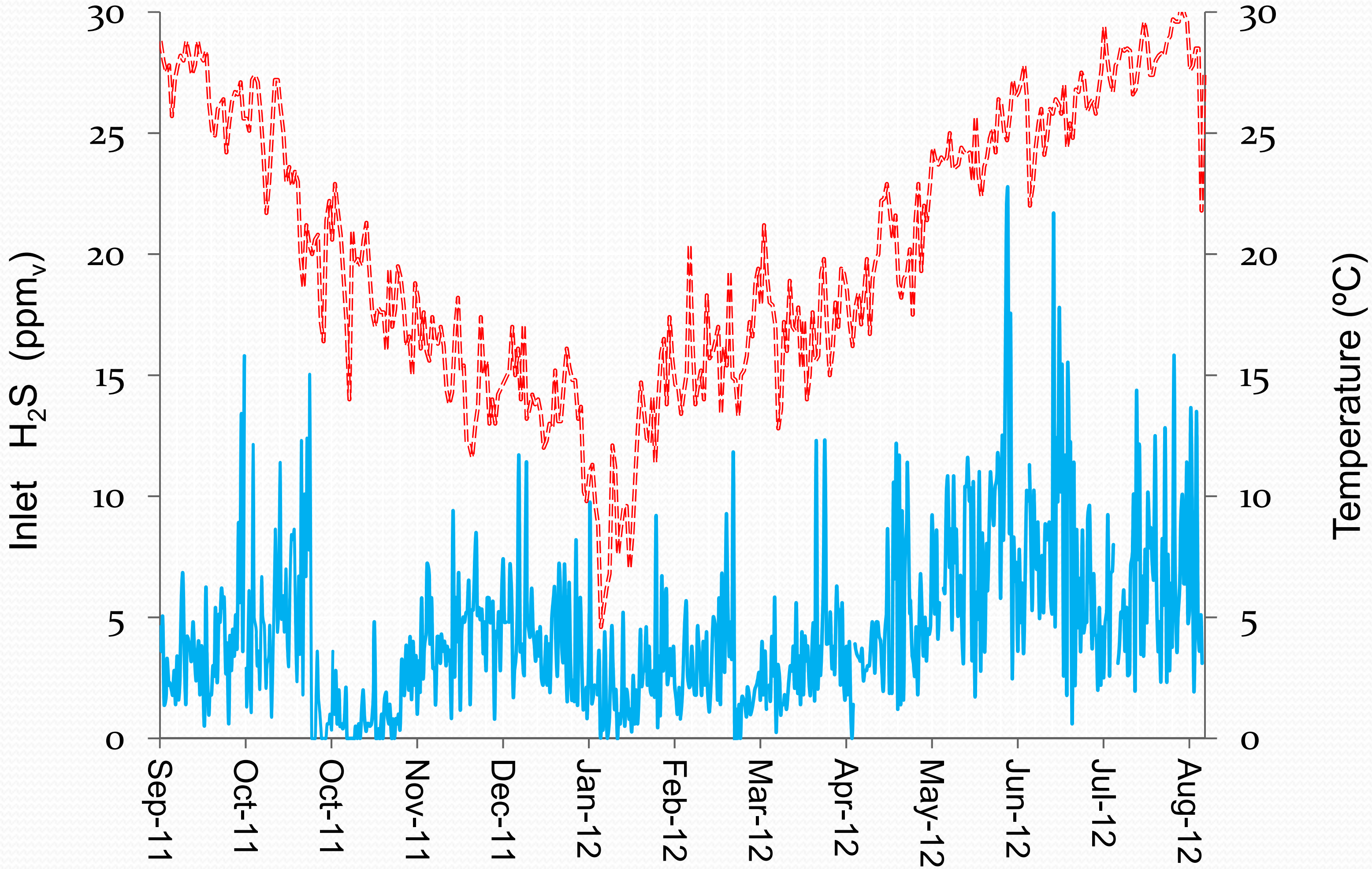
Clearly a minimum EBRT is needed for satisfactory results



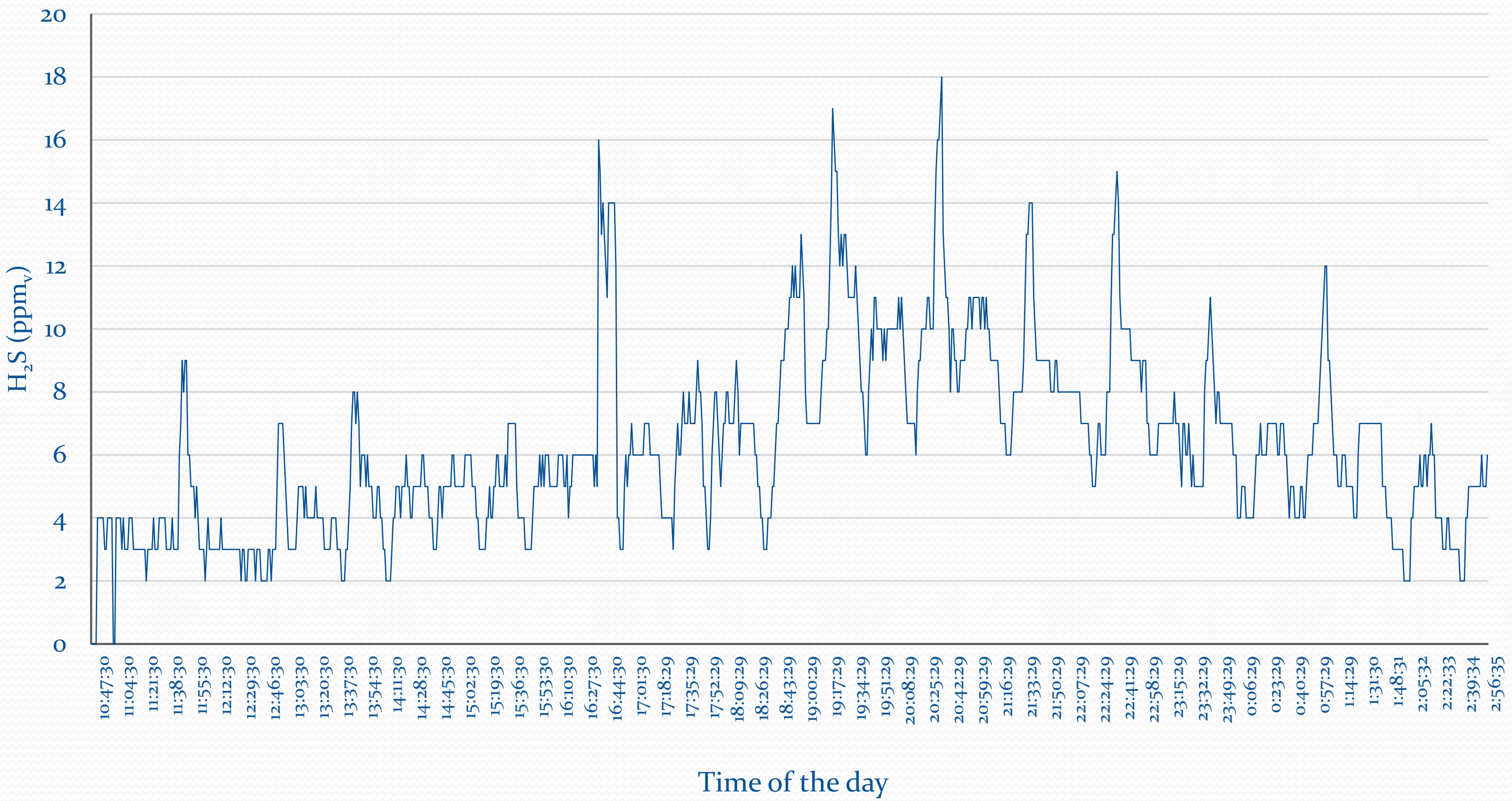
Current conditions at the deodorization facility at Cunit-Cubelles WWTP

Paràmetre	Valor
Polluted gas flowrate(Q_{in})	10,000 m³/h
Contact time (EBRT)	1.5 s/reactor 4.5 s/three reactors
Reactor volume (V)	4 m³
pH	6.5
Make-up water	0.4 m³/h
Recirculation	5 m³/h
Pollutants	H_2S, Volatile Organic Compounds
H_2S	2 – 30 ppm
VOCs	0 – 6 ppm
Liquid volume per reactor	1.8 m³

The proposed solution should alson account with seasonal variations....



...and hourly variations!!



- **Low loads during the morning until the afternoon**
- **High loads during the late afternoon**

Conversion protocol of chemical scrubbers into BTFs at the Cunit-Cubelles WWTP

Conversion performed by ECOTEC under the supervision of UPC and UAB

Main modifications

- Packing material replacement
- Gas-liquid separator replacement
- Paclimg mat. Support replacement
- Pumps replacement (lower power)
- Flowmeters and valves
- pH and level controls
- Inoculation port placement
- Distribution liquid system replacement
- Pressure drop monitoring

Process monitoring

Sampling and monitoring protocols stablished

Daily monitoring of H_2S and COVs gas flowrate, T, %RH…

Weekly monitoring of the líquid phase

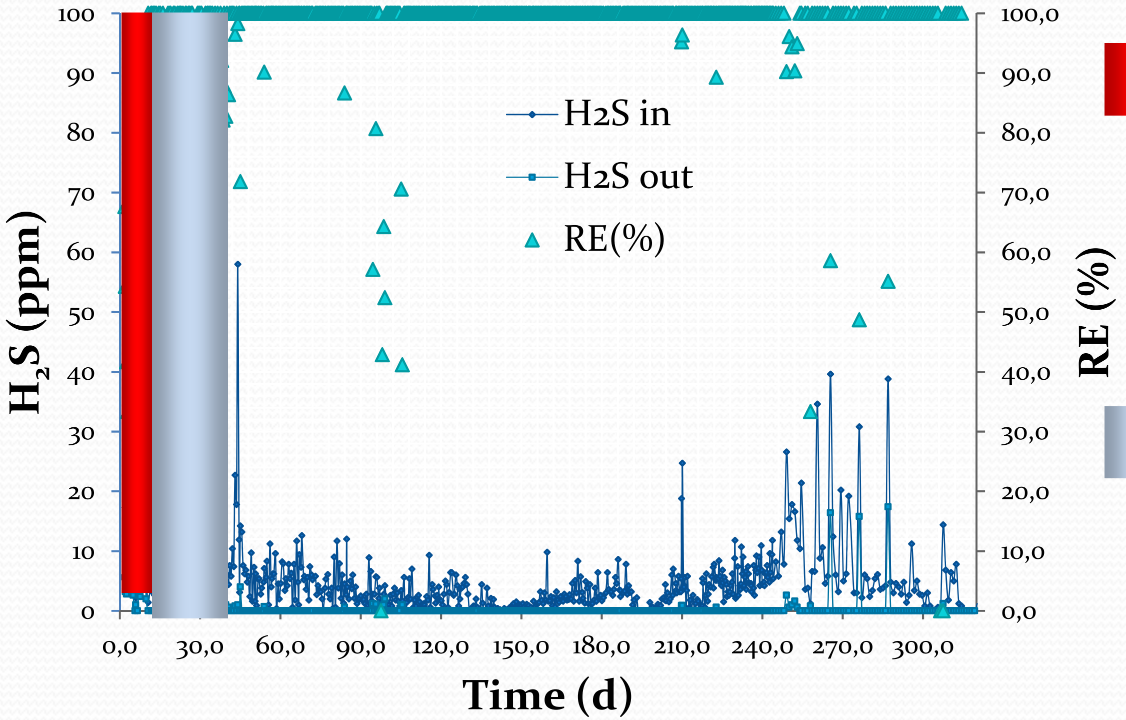
Monthly COVs screening

Monthly dynamic olfactometry measurements

ODOURNET
air quality and odour research consultants

Main results

Period: Oct. 2012 – Sept. 2013



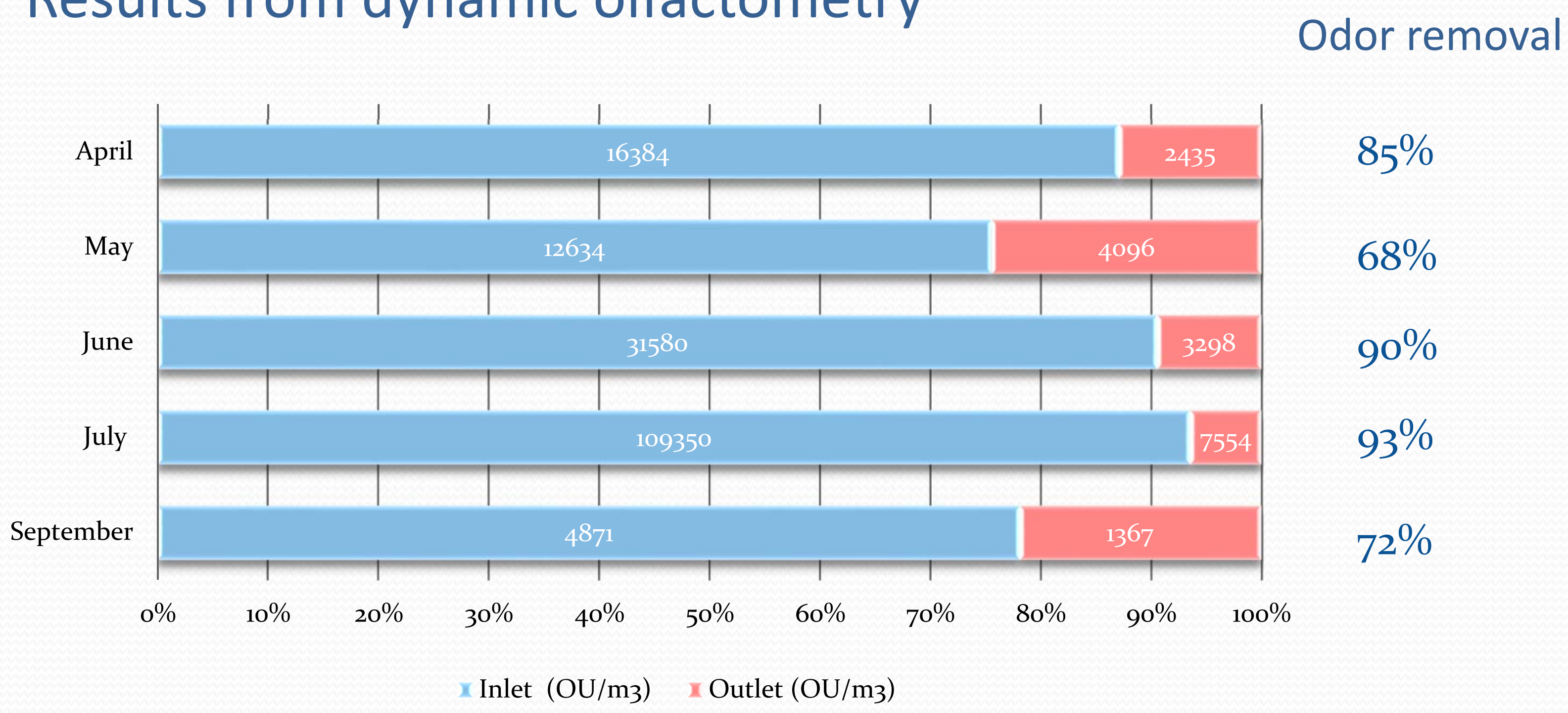
Start-up (30-70% RE)

Second phase (80-100% RE)

- **Start-up a bit slower tan pilot tests**
- **Average removal efficiency: RE >97%**
- **System able to face inlet load fluctuations**

Odor abatement

Results from dynamic olfactometry



- Average odor RE 81%: Higher odor concentration → higher RE
- *Number of odor complaints reduced to few punctual episodes*

Economic feasibility

Cost-Benefit analysis based in the amount of reagents needed for complete pollutants abatement.

Capital expenditure	26,850€
Current reagents consumption	34182€ per year
Payback Period	9 – 10 months

CASE STUDY 2
Biogas desulfurization with high performance Biotrickling Filters

Biogas as alternative energy source

Fossil fuels

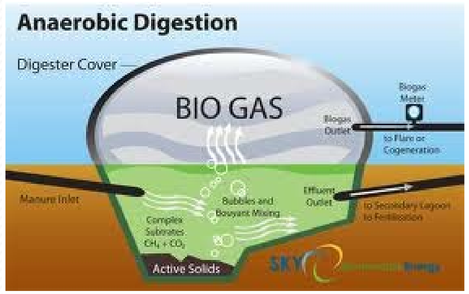
- Prices increase
- Scarcity

Technology innovation

- Energy recovery from wastes

Anaerobic Digestion

- Biogas production from organic wastes



Biogas

- Energy rich-effluent that can be used for:
- Electricity generation
- Heating or as a fuel

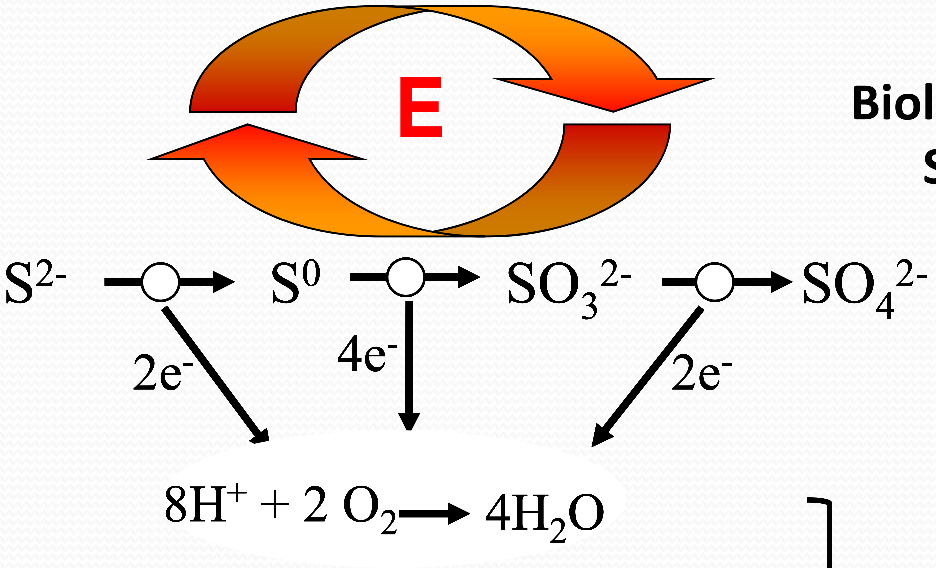
Biogas content

- Mainly : CH_4 and CO_2 + impurities: H_2S (0.1-2%), VOSCs

Energy Recovery from biogas

- Physico-chemical pre-treatments
- Biological pre-treatments

Hydrogen sulfide oxidation by chemoautotrophic bacteria



Biological H_2S oxidation carried out by Sulfide Oxidizing Bacteria (SOB)

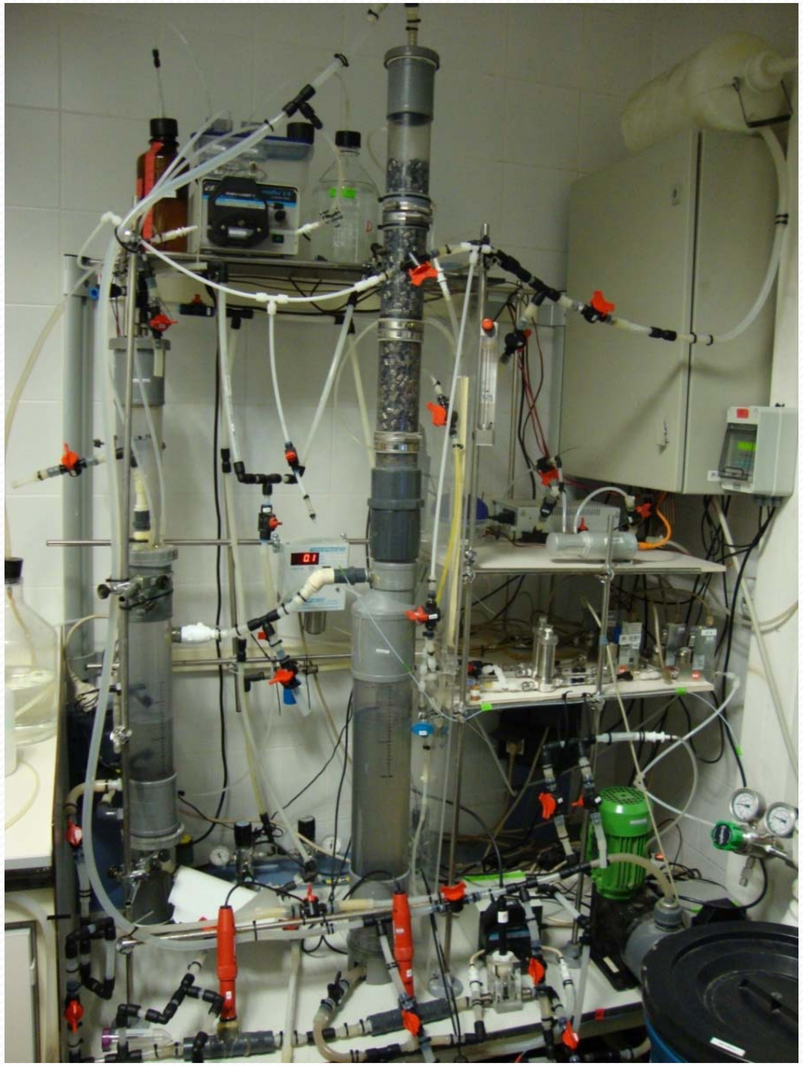
$$HS^- + 0.5\ O_2 \rightarrow S^0 + OH^-$$

$$S^0 + 1.5\ O_2 + H_2O \rightarrow SO_4^{2-} + 2\ H^+$$

$$HS^- + 2\ O_2 \rightarrow SO_4^{2-} + H^+$$

Limited oxygen leads to limited performance due to S^0 formation

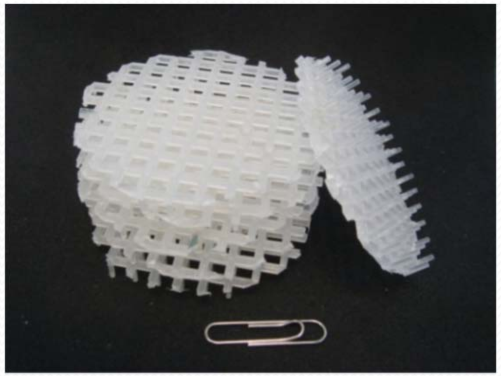
Where we did the work?



EXPERIMENTAL SETUP

TYPICAL OPERATING CONDITIONS

- Volume = 2.15 L
- Gas residence time (EBRT) = 180 s
- Liquid residence time = 10h
- **More than 5 years under continuous operation**
- pH control (6.0 and 2.0)
- $[H_2S]_{in}$ = **2000** to 10000 ppm_v
- Packed with:
  - Inox Pall rings (10mm)
  - Plastic HD-QPack
- Inoculation with WWTP aerobic sludge



… but we also have done some work in full-scale biotrickling filters

2500 ppm_v H_2S; 83 m^3 biogas h^{-1}

Oxygen transfer and solids flushing

1” Pall rings

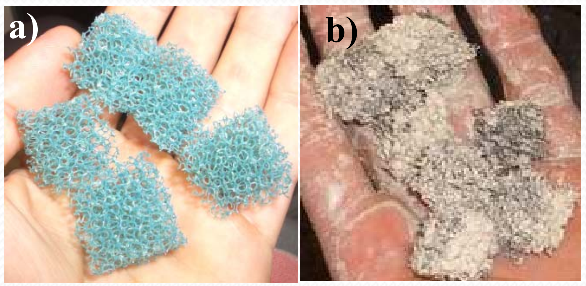
Acid pH (2.6) and pH control by make-up water

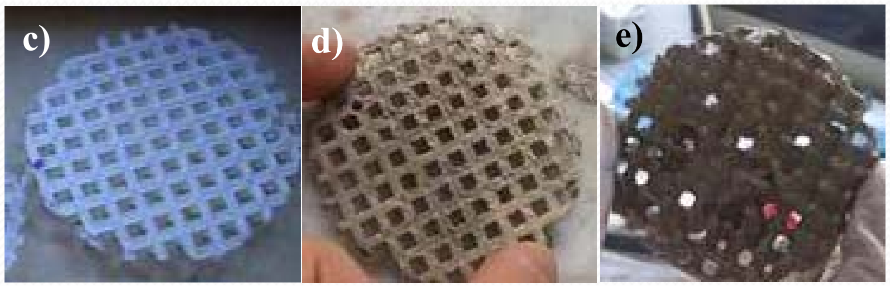
Some drawbacks observed…

Elemental S accumulation is the main bottleneck of the process for the treatment of high loads of H_2S

H_2S_{in} (ppm_v)	Load (g H_2S $m^{-3}h^{-1}$)	$O_2/H_2S_{supplied}$ (v/v)	$S\text{-}SO_4^{2-}/S\text{-}H_2S_{removed}$ (%)	$S\text{-}S^0/S\text{-}H_2S_{removed}$ (%)
3,000	74	5.3	60-70	28-38
6,000	155	2.6	20-30	68-78
10,000	259	1.6	3-4	94-95

(Fortuny et al, 2008, Chemosphere)





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

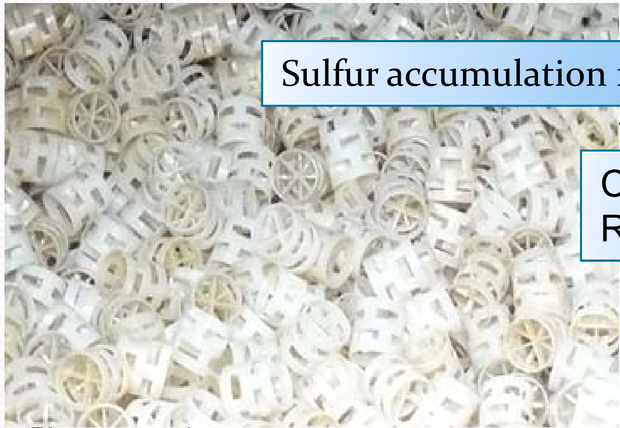
Leasons learned so far…

- It works!!! Robust process: long-term stability if periodically cleaned
- Packing material surface area is not critical
- Packing material structure plays a major role in S^0 flushing/biomass retention
- Cocurrent G/L flow pattern is slightly better that countercurrent
- H_2S removal at acid pH slightly improves H_2S EC
- At acid pH microbial diversity is lower but less competition/problems occur
- Maximum performance EC_{max}= 210-220 g H_2S/m^3h increasing concentration
- Key factor: oxygen supply
  1. If large, excessive biogas dilution
  2. If short, excessive S^0 production

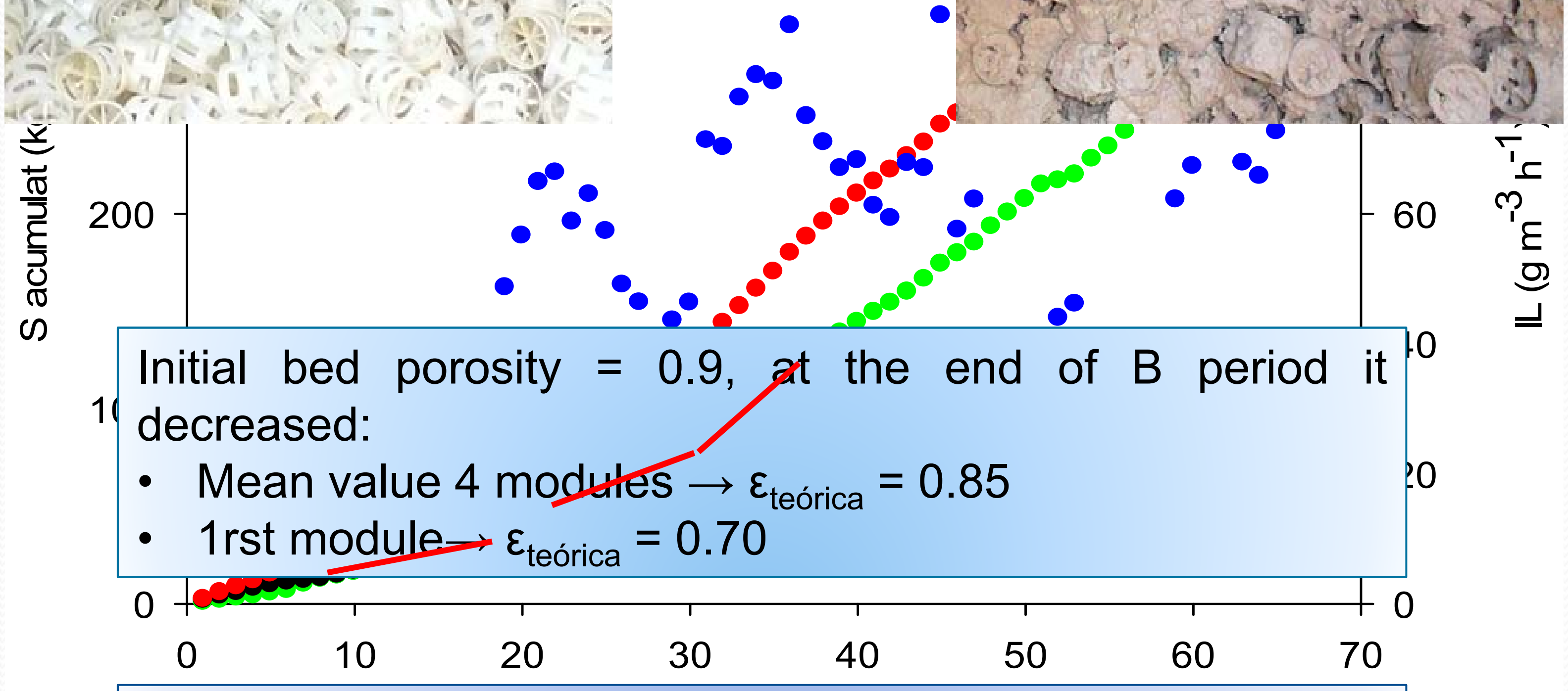
What is limiting reactor performance at high concentrations?

Oxygen G-L mass transfer

Sulfur accumulation from 1.2 to 4.0 kg day^{-1}



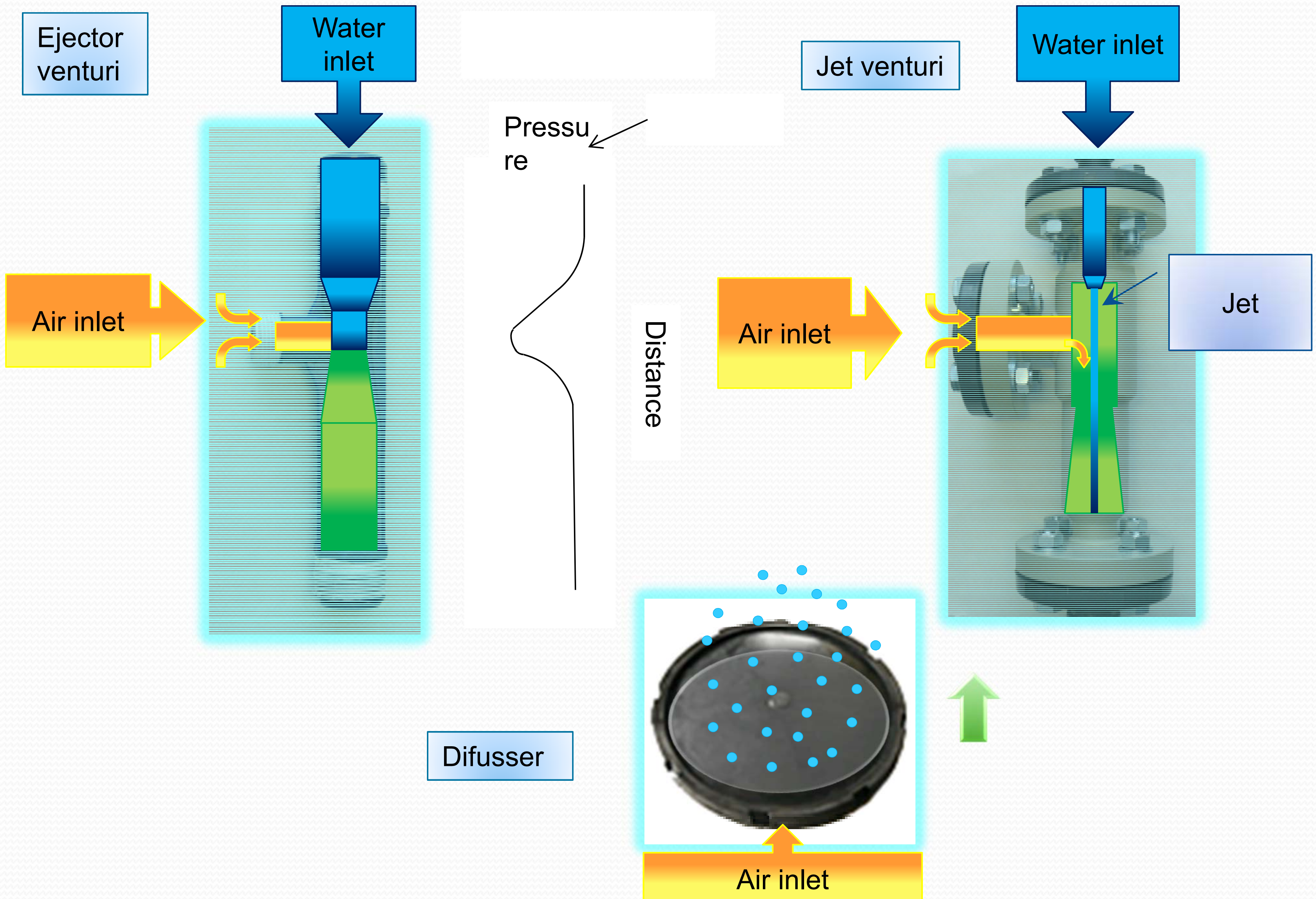
$C_{G,H2S,out}$ > 500 ppm$_v$
RE 71 %



Initial bed porosity = 0.9, at the end of B period it decreased:

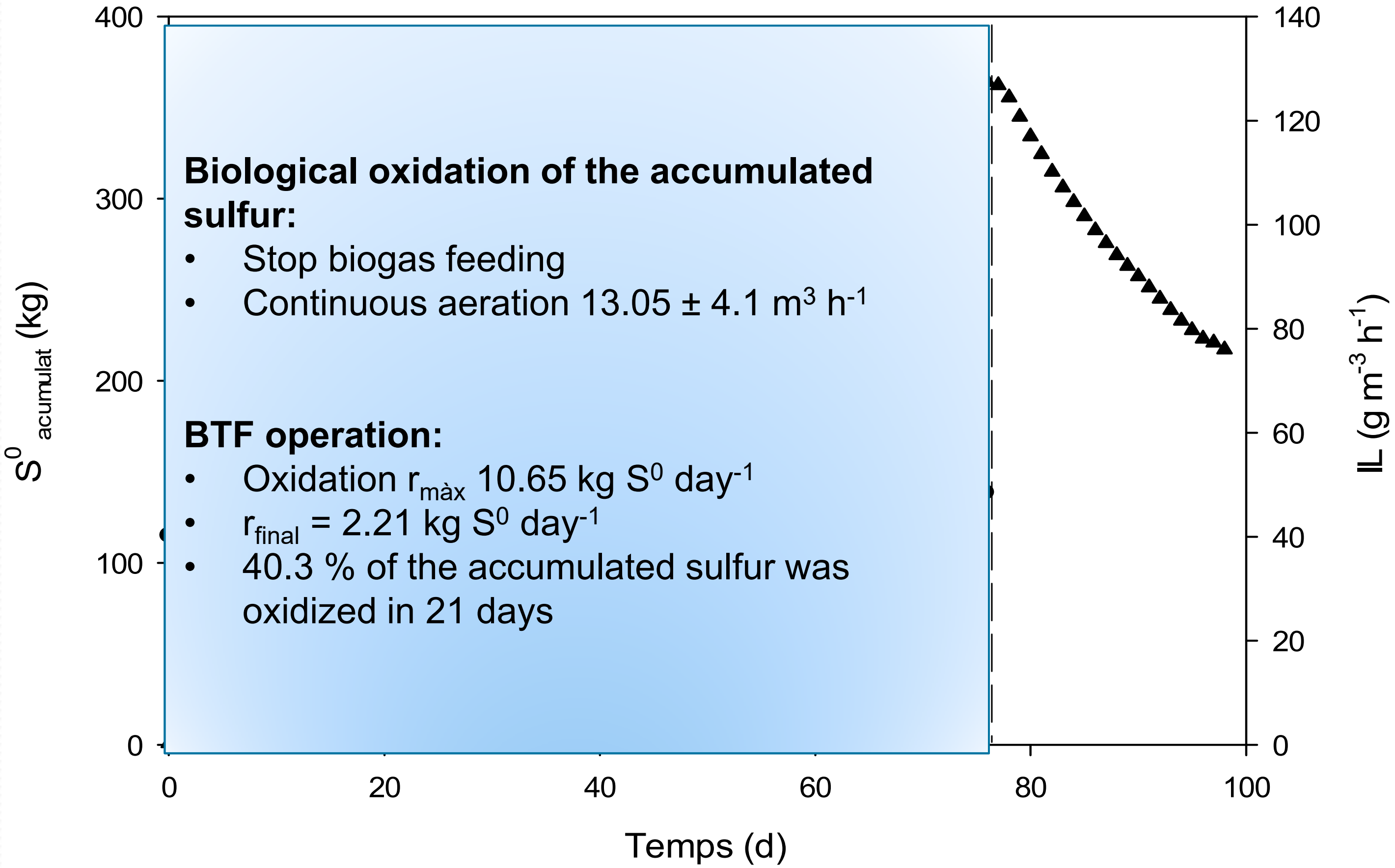
- Mean value 4 modules → $\varepsilon_{teórica}$ = 0.85
- 1rst module → $\varepsilon_{teórica}$ = 0.70

Oxigen mass transfer needs to be improved in order to minimize elemental sulfur production


Ejector venturi
Water inlet
Pressu re
Distance
Air inlet
Jet venturi
Water inlet
Jet
Air inlet
Difusser
Air inlet

Variable	Aeration system		Units
	Compressor (D2)	Jet venturi (G)	
pH	1.88 ± 0.07	1.82 ± 0.02	-
Air Flowrate	22.1 ± 5.7	4.7 ± 2.1	$m^3 h^{-1}$
DO	1.4 ± 1.1	1.5 ± 1.6	$mg l^{-1}$
% CH4	51 ± 6	57 ± 3	% v/v
Water consumption	4.3 ± 1.0	7.6 ± 2.7	$m^3 d^{-1}$
Biogas Flowrate	1875 ± 397	1746 ± 434	$m^3 d^{-1}$
H_2S in	2556 ± 334	2468 ± 398	ppm_v
H_2S out	58 ± 158	29 ± 16	ppm_v
Sulfate	3351 ± 551	2040 ± 408	$mg SO_4^{2-} l^{-1}$
RE	98 ± 7	99 ± 1	%
EC	72 ± 22	66 ± 18	$g m^{-3} h^{-1}$
Inlet Load	78 ± 23	67 ± 20	$g m^{-3} h^{-1}$
Ratio O_2/H_2S	23 ± 2	5 ± 1	$mol O_2 mol H_2S^{-1}$
%Conversion to sulfate	52 ± 19	69 ± 43	%

Periodic elemental sulfur oxidation to avoid reactor clogging



Biological oxidation of the accumulated sulfur:

- Stop biogas feeding
- Continuous aeration 13.05 ± 4.1 $m^3\ h^{-1}$

BTF operation:

- Oxidation $r_{màx}$ 10.65 kg S^0 day^{-1}
- r_{final} = 2.21 kg S^0 day^{-1}
- 40.3 % of the accumulated sulfur was oxidized in 21 days

Average sulfur conversion of 48 %, 364 kg at the end of period

Take home ideas:

Bioreactors work and are very competitive vs physical-chemical processes

Further research is needed to expand the potential fields of application of gas-phase bioreactors

G-L mass transfer and biology are the key aspects in reactors performance and design

Multidisciplinary approaches and tools (biology, monitoring, modelling...) are needed to improve knowledge

Some public funding

Desarrollo y caracterización de biorreactores para el tratamiento biológico de efluentes gaseosos (CICYT PPQ2003-02482). 2003-2006

Tratamiento por biofiltración de efluentes odoríferos contaminados con compuestos orgánicos e inorgánicos volátiles (MMA 183/2006/3-11.1). 2006-2007

Tratamiento integral de efluentes gaseosos en instalaciones industriales mediante biorreactores (CICYT CTQ2006-14997-C02). 2006-2009

Desulfuración de gases ricos energeticamente mediante biofiltros percoladores: desarrollo y optimizacion del proceso en condiciones anoxicas y aerobias (CICYT CTM2009-14338-C03). 2010-2012

Monitorizacion, modelizacion y control para la optimizacion de biofiltros percoladores de desulfuracion anoxicos y aerobios (CICYT CTM2012-37927-C03). 2013-2015

Desarrollo de un proceso integral de tratamiento de SOx y NOx procedentes de gases de combustión orientado a su valorización (MINECO CTQ2015-69802-C2). 2016-2018

Developing on line tools to monitor, control and mitigate GHG emissions in WWTPs (Horizon 2020 Sub-programme Call: H2020-MSCA-RISE-2014 , Project ID: 645769). 2015-2019

Some private funding

Estudio de la viabilidad de la eliminación de sulfuro de hidrógeno a altas concentraciones mediante biofiltración. (Tecnium, Casals Cardona Industrial). 2005-2006

Optimización de rellenos utilizables como soporte para la biofiltración de corrientes gaseosas (Sistemas y Tecnologías Ambientales). 2005-2006

Conversión de lavadores químicos en biofiltros percoladores para el tratamiento de gases residuales (Ecotec S.A.) 2009-2011

Optimización de Compostaje, Biosecado y Olores (Urbaser S.A.) 2013-2015

Nuevas formulaciones para la obtención del pigmento azul ultramar (Grupo Ferro Inc.) 2015-2017

Biofiltración de emisiones gaseosas: fundamentos y aplicaciones

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