Universitat de Girona

# Aplicació de tecnologies bio-electroquímiques al tractament d'aigües:

## recuperació de nutrients i compostos de valor afegit

Dr. Jesús Colprim Galceran (J.Colprim@lequia.udg.cat)

lequia UdG ECO-INNOVATIVE WATER SOLUTIONS

tecnio catalonia ACCIÓ Generalitat de Catalunya

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# Qui som?

lequia UdG ECO-INNOVATIVE WATER SOLUTIONS

Universitat de Girona

Agència de Gestió d'Ajuts Universitaris i de Recerca (AGAUR)

tecnio catalonia ACCIÓ Generalitat de Catalunya

- Un grup de recerca de la UdG (GRCT0044) creat el 1992 y centrat en la recerca bàsica i aplicada en solucions eco-innovadores en el camp de l'aigua.
- Reconeguts per la Generalitat de Catalunya com a "Grup Consolidat" (2014-SGR-1168)
- Centre TECNIO. TECNIO es una xarxa de recerca aplicada i transferència de tecnologia a Catalunya..

**Línies de Recerca**

- Disseny, operació i control de processos avançats per al tractament biològic d'aigües residuals urbanes i industrials.
- Valorització de recursos dins del binomi Aigua Energia.
- Sistemes de Suport a la presa de decisions ambientals (EDSS)
- Processos avançats d'adsorció/oxidació per al tractament d'eluents líquids i gas.

# Col·laboració estratègica

- Recerca a la **UdG**:
  Jesús Colprim, Manel Poch, Maria Martín, Marilós Balaguer, Sebastià Puig

- Recerca al **ICRA**:
  Ignasi Rodriguez-Roda, Joaquim Comas

TECNIO Be tech. Be competitive
Universitat de Girona
lequia UdG ECO-INNOVATIVE WATER SOLUTIONS

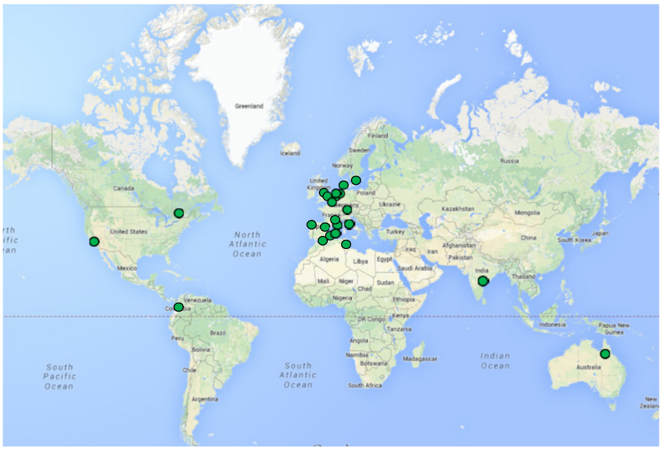
**40** persones, **17** investigadors amb Doctorat, equip **multidisciplinar**

# Cooperació internacional

lequia UdG ECO-INNOVATIVE WATER SOLUTIONS

University of Queensland (Australia)
NIT (India)
U. Nacional de Colombia (Colombia)
Université de Sfax (Tunis)

University of California, Irvine (USA)
U. Laval (Quebec, Canada)
UFZ (Germany)
TU Delft (The Netherlands)
Ghent University (Belgium)
DTU (Denmark)
Cranfield University (UK)
Exeter University (UK)
INRA (Narbonne, France)
Wageningen University (The Netherlands)
University of Pavia (Italy)



USC (Galicia, Spain)
ICRA (Catalonia, Spain)
PSA (Andalucía, Spain)
UV (Valencia, Spain)
UPC (Catalonia, Spain)
CEIT (Basque Country, Spain)

## Cooperació internacional

## Estudis Universitaris

Universitat de Girona

**Facultat de Ciències (Títols Oficials)**
**Estudis de GRAU (4 anys)**

- Grau en Biotecnologia
- Doble Grau en Biotecnologia-Biologia
- Grau en Ciències Ambientals
- Grau en Química

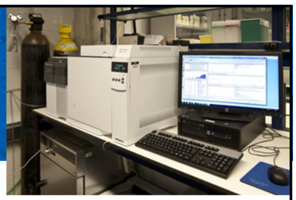
**Estudis de Màster (1 any):**

- Màster en Ciència i Tecnologia de l'Aigua.

**Estudis de Doctorat (3 anys):**

- Doctorat en Ciència i Tecnologia de l'Aigua

## LEQUIA en nombres...



- Des de **1992**
- **550 m2** laboratoris I plantes pilot
- Plates pilot sobre el terreny
- Captació de recursos 2011-2014: **1,4 M€ /any** (24% fons privats)
- **3 patents industrials**
- **1 spin-off:** SISLtech S.L. (www.sisltech.net), fundada el 2003
- Director: Dr Jesús Colprim (J.Colprim@lequia.udg.cat)

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## Instal·lacions

- **Plantes pilot** completament instrumentades amb diferents configuracions per al tractament d'aigües residuals a escala **laboratori** i **industrial** (on-site)
- Instrumentació per al **seguiment i control de plantes de tractament d'aigües residuals**.
- **Laboratori** d'anàlisi química
- Fotoreactors per a **processos d'oxidació avançada**.
- Programari per a la **modelització ambiental i anàlisi del cicle de vida**.
- Identificació de poblacions microbianes mitjançant **tècniques moleculars** (FISH, SEM, PCRs)

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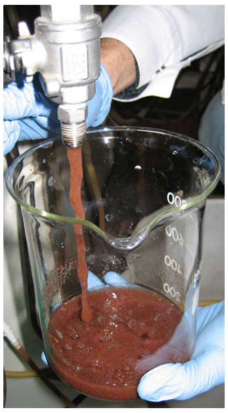
# Instal·lacions

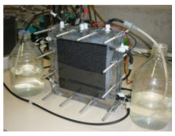
# Research expertise

## Design, operation and control of advanced processes for the biological treatment of urban and industrial wastewaters



- **Industrial and urban WWTP** technologies
  - Assessment of WWTPs efficiency
  - SBR for C:N:P removal
  - MBR processes: SmartAirMBR®
  - Sludge reduction: Biminex®
  - GHG emissions ($N_2O$ study and mitigation)
- Development of **advanced technologies**:
  - Partial Nitratation, anammox: Panammox® process
  - Phosphorus recovery (struvite)
  - Main stream one stage anammox

# Research expertise
Valorization of resources within the water-energy nexus



**BioIElectrochemical Systems/Technologies (BES/T)**

- Direct electricity production: **Microbial Fuel Cells (MFC)**
  - Simultaneous C and N removal (industrial/urban wastewater)
- **Biocathodes** potential:
  - **Microbial Electro Synthesis (MES)**
    - Biogas upgrading: conversion of $CO_2$ to $CH_4$
    - Carboxylic pathway: $CO_2$ to Acetate and chain elongation
  - **Groundwater Pollutants reduction**:
    - Nitrate removal from groundwater, NoNit®
    - Sulphate removal
    - Arsenic removal

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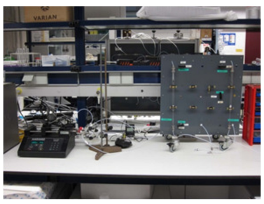
# Research expertise
Advanced adsorption/oxidation processes for the treatment of gas and liquid effluents



- Advanced **adsorption and oxidation processes**
  - **Activated carbon** form excess sludge
- Testing and characterisation of **adsorbent materials**
  - H2S removal
  - Siloxanes adsorption over AC
  - AC regeneration (from siloxanes/$H_2S$)
- Development of **biogas analysis**
  - siloxanes, odorous sulphur compounds, VOC

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# Research expertise
## Environmental Decision Support Systems (EDSS)

- Knowledge management and development of multi-criteria **environmental decision support systems (EDSS)**
- Integration of **artificial intelligence (AI) techniques with conventional modelling techniques and control algorithms** to manage complex environmental systems
- Integrated control of the **urban water cycle** (sewer system, WWT plant and receiving media) to improve the ecological status of water bodies.

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# Our approach

**Environmental-health issues**
- Contaminated water
- Urban/industrial wastewater
- Air pollution

**Leading edge technologies**
- Aerobic granular sludge
- PANAMMOX
- Bioelectrochemical Systems
- Nutrient recovery

**Products**
- Drinking water
- Regenerated water
- Biofuels
- Bioelectricity
- Organic fertilizers

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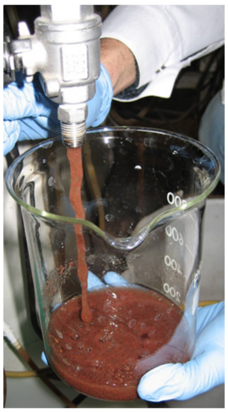
# Research examples

BNR: Panammox® process; Bioelectrochemical Technologies



- Industrial and urban WWTP technologies
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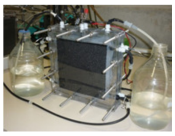
# Research examples

BNR: Panammox® process; BioelectrochemicalTechnologies



**BiolElectrochemical Systems/Technologies (BES/T)**

- Direct electricity production: Microbial Fuel Cells (MFC)
  - Simultaneous C and N removal (industrial/urban wastewater)

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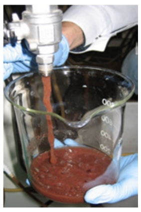
# Research examples

BNR: Panammox® process; Microbial exoelectronic Technologies



**BNR** autothophic nitrogen removal**:**

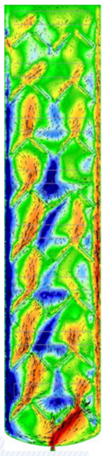
- **Partial Nitratation, anammox:** Panammox® process

**Biocathodes** potential:

**Microbial Electro Synthesis (MES)**
Biogas upgrading: conversion of $CO_2$ to $CH_4$
Carboxylic pathway: $CO_2$ to Acetate and chain elongation

**Groundwater Pollutants reduction**:
Nitrate removal from groundwater, NoNit®

**CFD applied to innovative technologies**



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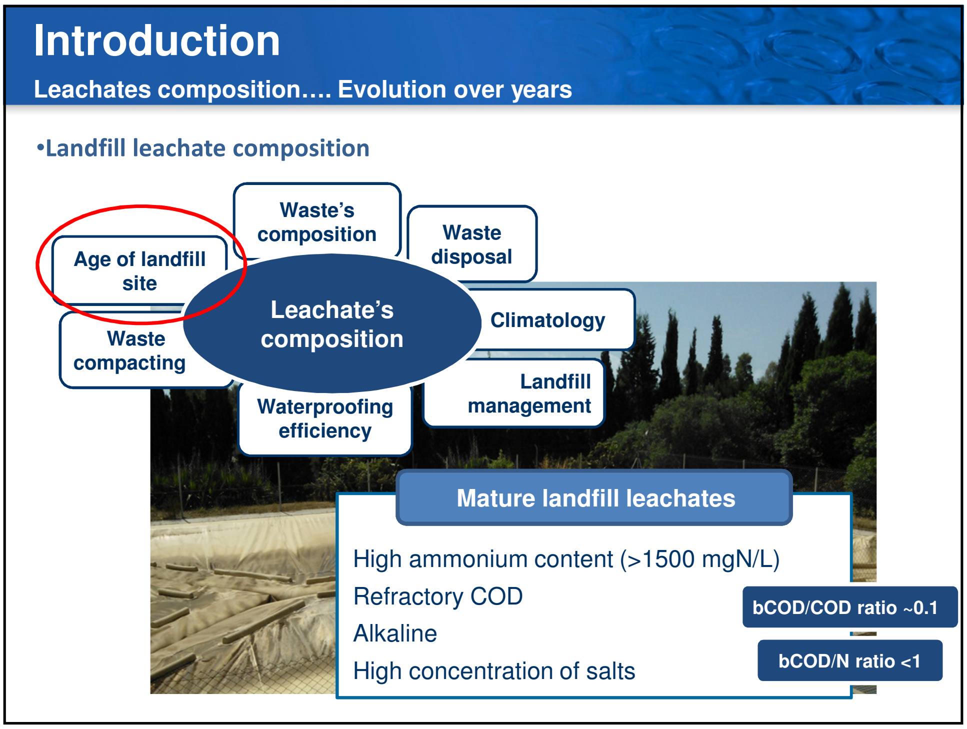
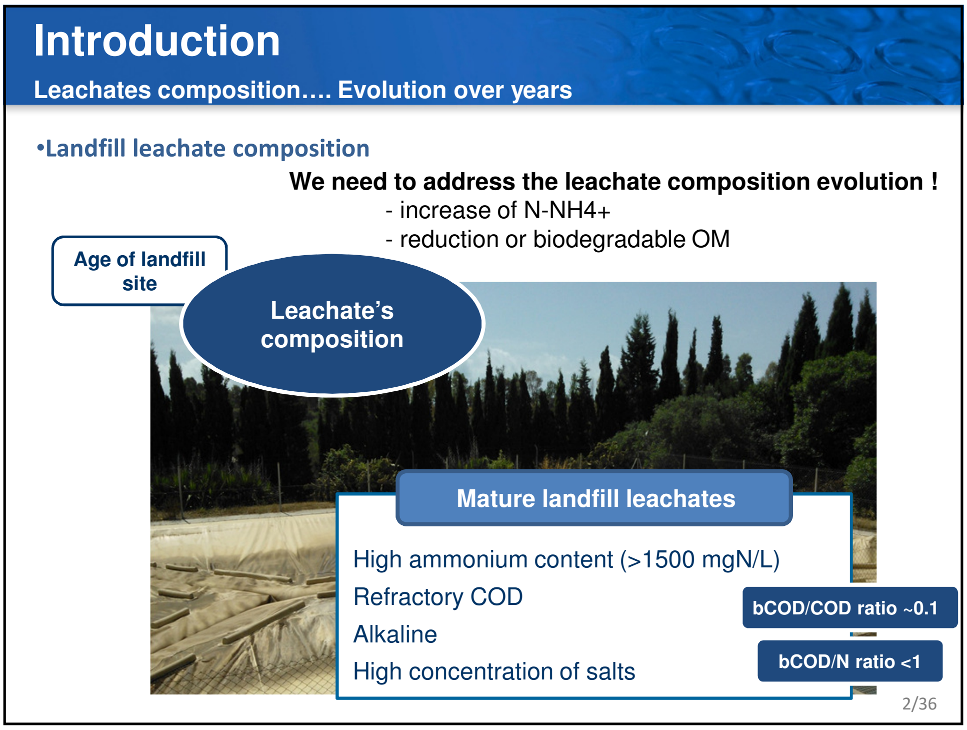
# Panammox® Process

Industrial wastewater: the case of **landfill leachates**

- **What about leachates?** (from landfill)
  - Biodegradable Municipal Wastes should be diverted from landfill
    - At EU, up to 75%-reduction (1995-2006)
    - Reduction of the total number of landfills (uncontrolled ones)
  - There is no evidence that the EU Landfill Directive reduced MW production
  - Landfill rates indicate that existing capacity in most countries is sufficient for next 20-30 years
- **Leachates from MW will remain for years and thus…**

**The production of landfill leachates is one of the main environmental concerns in landfill facilities. Treatment and management is required, even after closure of landfill sites.**


Introduction
Leachates composition…. Evolution over years
•Landfill leachate composition
Waste's composition
Waste disposal
Age of landfill site
Leachate's composition
Climatology
Waste compacting
Landfill management
Waterproofing efficiency
Mature landfill leachates
High ammonium content (>1500 mgN/L)
Refractory COD
Alkaline
High concentration of salts
bCOD/COD ratio ~0.1
bCOD/N ratio <1


Introduction
Leachates composition…. Evolution over years
•Landfill leachate composition
We need to address the leachate composition evolution !
- increase of N-NH4+
- reduction or biodegradable OM
Age of landfill site
Leachate's composition
Mature landfill leachates
High ammonium content (>1500 mgN/L)
Refractory COD
Alkaline
High concentration of salts
bCOD/COD ratio ~0.1
bCOD/N ratio <1
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# Introduction

## Concerns on landfill leachates treatments

**Conventional treatment**

**Biodegradable OM** and **Nitrogen** removal by biological processes, **External carbon source** and ammonia **stripping**

- External carbon source
- Energy consumption
- pH adjustment

**Refractory COD** removal by **membrane filtration** techniques

- Energy consumption
- Highly concentrated rejection

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# Introduction

## Concerns on landfill leachates treatments

| Conventional treatment | Alternative treatment |
|---|---|
| **If no external OM....** | |
| **Nitrogen** removal by ammonia **stripping** → | Combined **PN/Anammox** process (2-step process) |
| **Refractory COD** removal by **membrane filtration** techniques → | Advanced oxidation processes **(AOPs): (Photo-) Fenton** |

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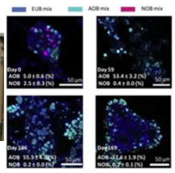
# Our previous experience

## PN-Anammox processes

### PN: Partial-Nitritation process

- **Stable** long term operation of PN-SBR processes
- **Step-feed** is better for optimal alkalinity use.
  - NOB supression by FA/FNA inhibition.
- Available **$HCO_3^-$:$NH_4^+$ ratio** controls the $NH_4^-/NO_2^-$ ratio
- **Rapid start-up** with raw landfill lechate
- **Removal of bCOD** prior to anammox process



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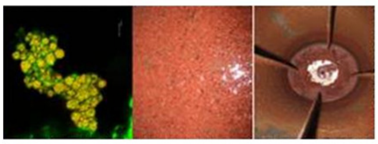
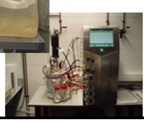
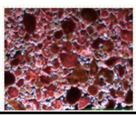
# Our previous experience

## PN-Anammox processes

### Anammox process

- **Start-up and enrichment** of anammox biomass without seeding
- **Adaptation** from mineral medium to real landfill leachate matrix
- Coexistence of **anammox and heterotrophic** bacteria
- Impact of **leachate matrix** on SAA
- **Granular** processes (SBR)

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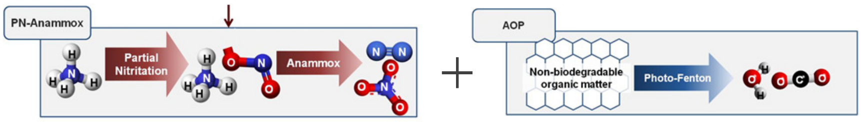
# Aim: From Lab to Full Scale

Coupling **2-step PN-Anammox process with AOP**

- **N removal**
- **refractory COD removal**




Lab → Pilot → Full scale

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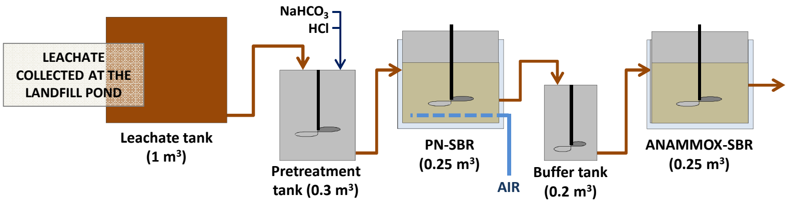
# Pilot plant: description

## Treatment of landfill leachates in 2-step PN-Anammox

- **Pilot plant scheme**




**PN-SBR:** 25°C; DO set-point at 2 mg $O_2$ $L^{-1}$; no pH control
**Anammox SBR:** 35°C; $pH_{max}$ set-point at 7.8

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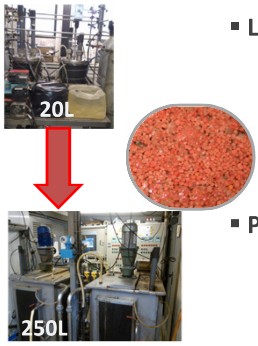
# Pilot plant: results

**From lab to pilot-scale:** Start up of the Anammox-SBR




- **Lab-scale anammox SBR → Strictly controlled conditions**
  - Synthetic influent
  - $N_2$ flushing
  - Reactor completely sealed to keep anoxic conditions

- **Pilot-scale anammox : simulation of start-up conditions**
  - No use of $N_2$ gas
  - Reactor not completely sealed
  - Inoculation with a very low amount of biomass

**Previous studies**
✓**Feasibility** of PN-Anammox process

**Challenges**

- Start-up with **little amount** of seeding sludge
- Possible impact of **high conductivity** levels
- **Coupling** directly with PN-SBR

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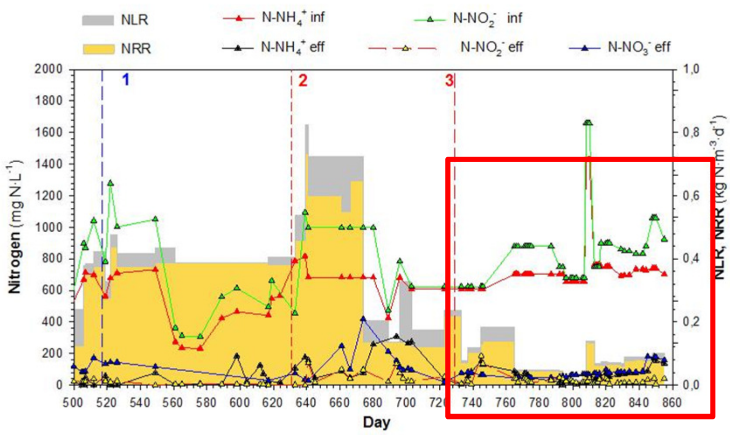
# Pilot plant: results

**Landfill leachate treatment in the Anammox-SBR**

•**Anammox-SBR performance: Phase 2-Landfill leachate**

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# Pilot plant: summary

## Landfill leachate treatment by PN-Anammox

- operation with **real leachate**
- **Stable** and high N-removal efficiency (>86%)
- **bCOD removed** in first stage (PN), anammox secured
- Stable specific N removal rate **0.4 Kg N/Kg SSV/day**

**However: Impact of the leachate matrix on specific anammox activity (SAA)**

SAA of the biomass from the anammox reactor adapted to leachate
- In mineral medium: 0.8-1.1 g $N_2$-N $g^{-1}$ VSS $d^{-1}$
- In leachate matrix: <0.4 g $N_2$-N $g^{-1}$ VSS $d^{-1}$

**Need for process with high biomass retention capacity to work at high VSS**

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# Full-scale

**Selection criteria**
- Maturity of leachate
- bCOD/N ratio (<0.5)
- Existing facilities
- Discharge requirements
- Location
- Type of wastes
- Years to closure


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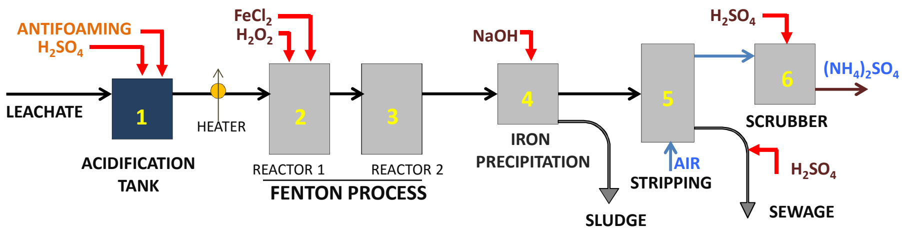
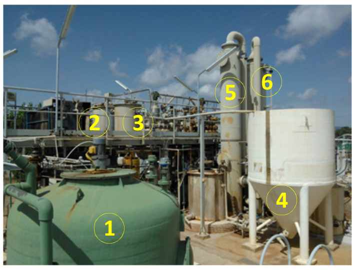
# Full-scale




**Current treatment**
**Fenton + $NH_3$-stripping**

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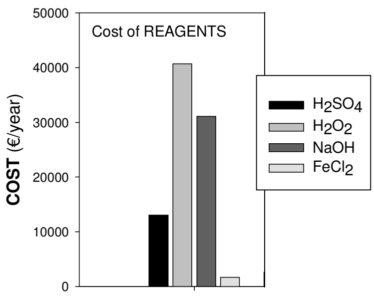
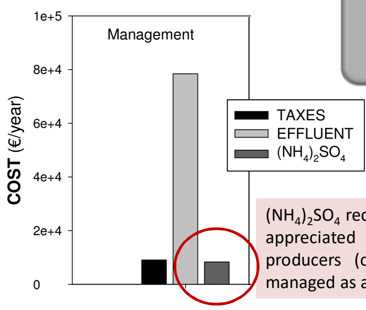
# Full-scale: Economics

To convince the plant manager….

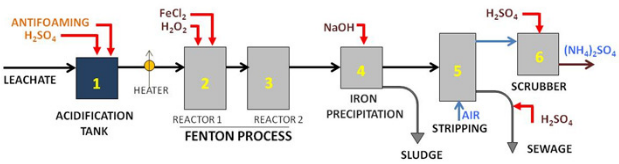
## Cost of leachate treatment by $NH_3$-stripping




By stripping: 28.8 €/m³

$(NH_4)_2SO_4$ recovered is not appreciated by fertilizer producers (origin) and is managed as a waste

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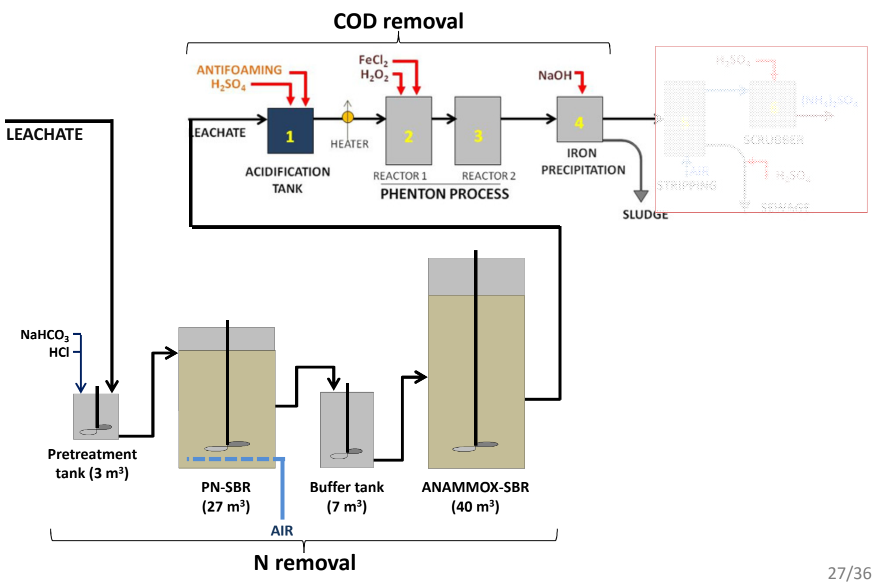
# Full-scale: implementation

**First PN-Anammox, second AOP**

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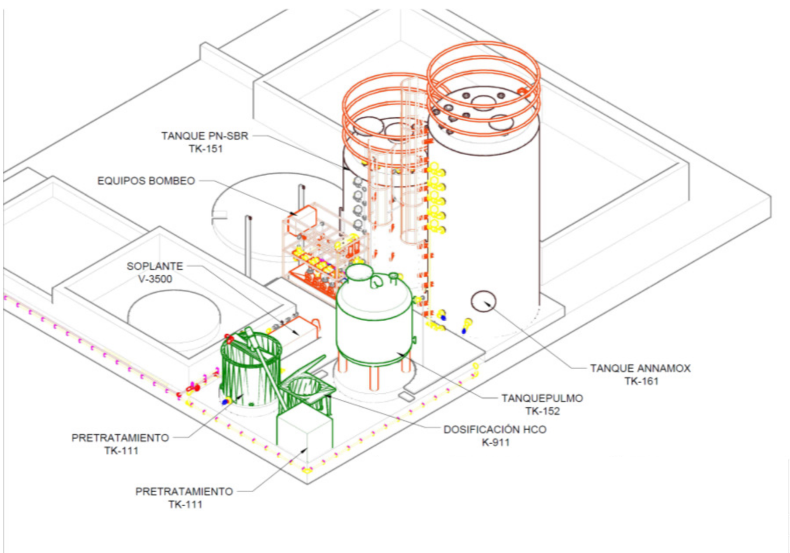
# Full-scale: engineering

**Designed to treat 19 m³ day⁻¹ of landfill leachate**



# Full-scale: P&I

**Designed to treat 19 $m^3$ $day^{-1}$ of landfill leachate**

**PN inoculation (April 2014)**

- Activated sludge from a municipal WWTP

**Operational conditions**

- DO set-point at 2.0 mg $O_2$ $L^{-1}$; Temperature control <20° C; $pH_{max}$=7.9

**Inoculation Anammox (July 2014)**

- 90% of the mixed liquor from anammox pilot plant
- Initial VSS of only 0.07 gVSS $L^{-1}$

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# Full-scale

## Status

- **PN-SBR full operational**
- **Anammox-SBR is at the enrichment phase of the start-up:**
  - **Treatment capacity from 0.025 kg N $d^{-1}$ to 1.00 kg N $d^{-1}$**
  - **Biomass from 0.07 g VSS $L^{-1}$ to 0.28 g VSS $L^{-1}$**

- **PN-SBR is treating up to 25 $m^3$ $d^{-1}$ of leachate,**
- **The PN effluent is partially by-passed directly to the AOP**

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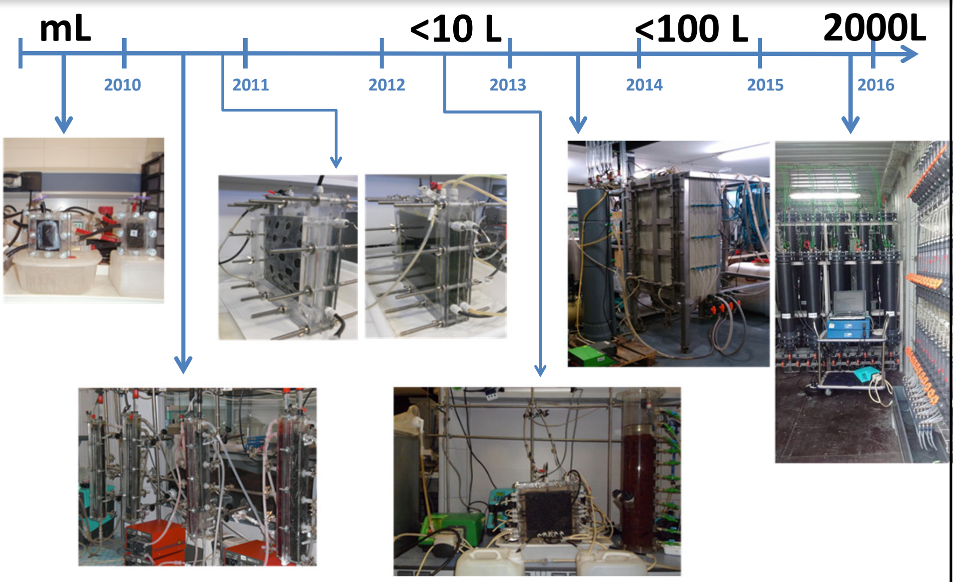
## BES: Research lines

Research on **water and wastewater treatment** (domestic/industrial) and **air polluted** treatment by applying bioelectrochemical systems.

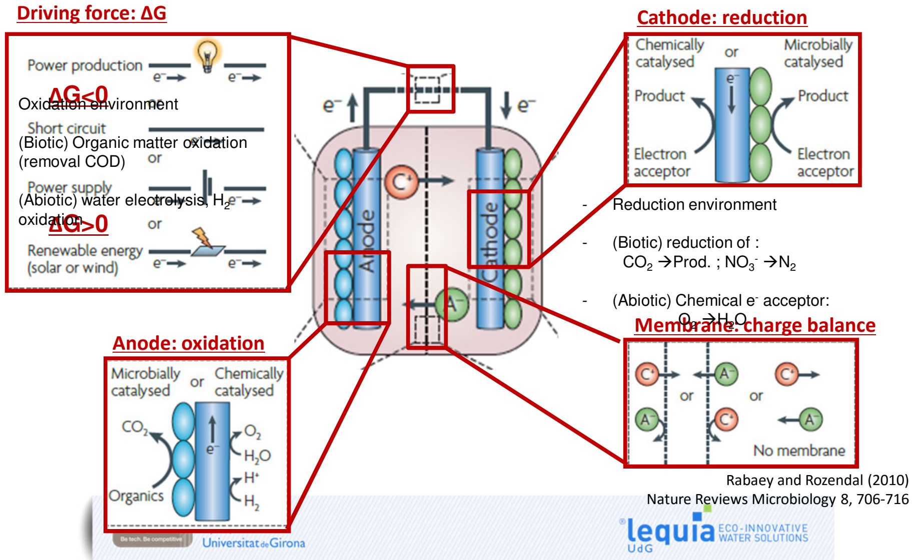
1. **Carbon dioxide** capture and transformation
2. Bioremediation of **contaminated groundwater** and surface water.
3. The effect of MFC architecture on simultaneous organic matter and nitrogen removal from domestic and **industrial wastewater**.

## Our story within BES



# Bioelectrochemical Systems (BES)

From where comes BES ?



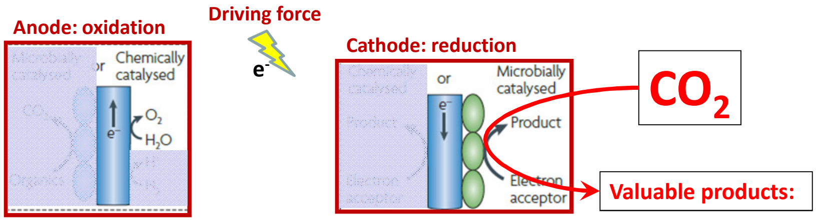

- Oxidation environment
- (Biotic) Organic matter oxidation (removal COD)
- (Abiotic) water electrolysis, $H_2$ oxidation

- Reduction environment
- (Biotic) reduction of : $CO_2$ →Prod. ; $NO_3^-$ →$N_2$
- (Abiotic) Chemical e⁻ acceptor: $O_2$ →$H_2O$

Rabaey and Rozendal (2010)
Nature Reviews Microbiology 8, 706-716

# Microbial electrosynthesis (MES)

Source and products within MES: a **biocathode reaction**

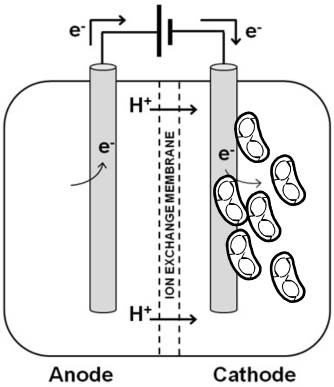



- **Carboxylic acids**: acetate, propionate, …
- **Methane**
- **Alcohols:** ethanol, butanol, …

**Why it works:**

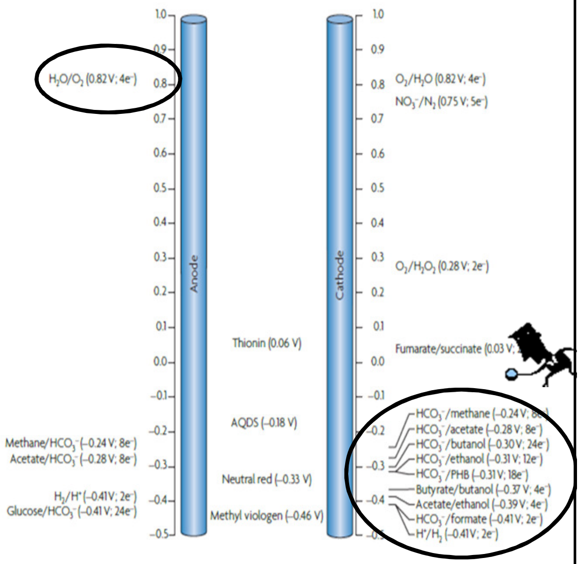
- Anode: **water oxidation**
- Cathode: $CO_2$ reduction, **biocathode**
- Energy: **power supply**
- Membrane: C/A membrane or membrane less (study)

## Microbial electrosynthesis



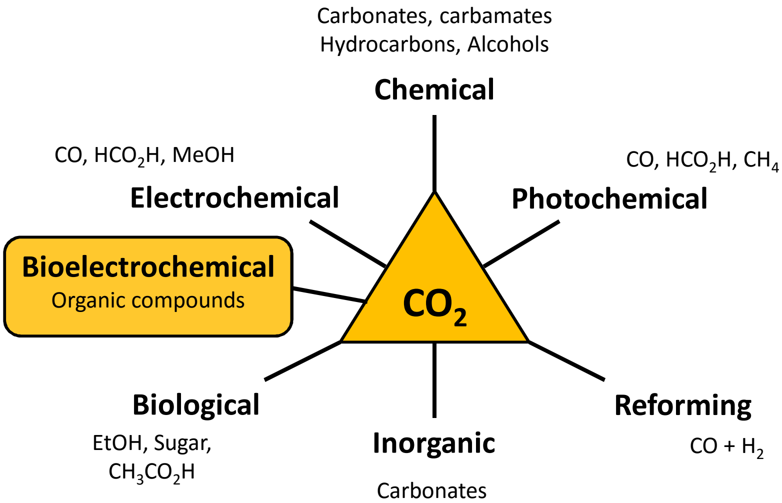

Ecell < 0
ΔG > 0
Non spontaneous

Energy required



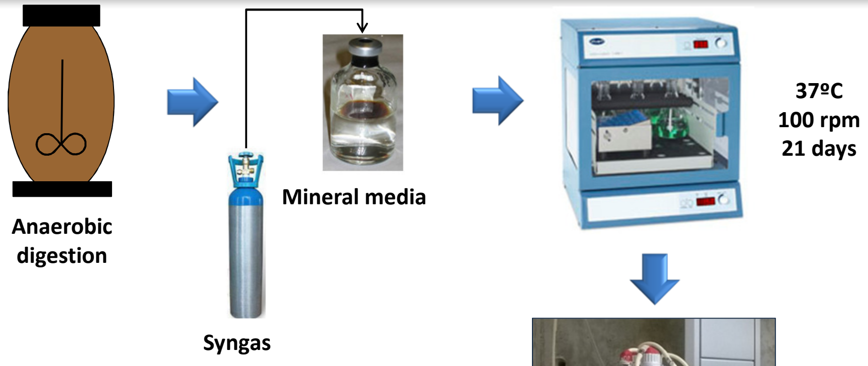

Rabaey and Rozendal, 2010. *Nature Rev Microbiol*

## $CO_2$ transformation



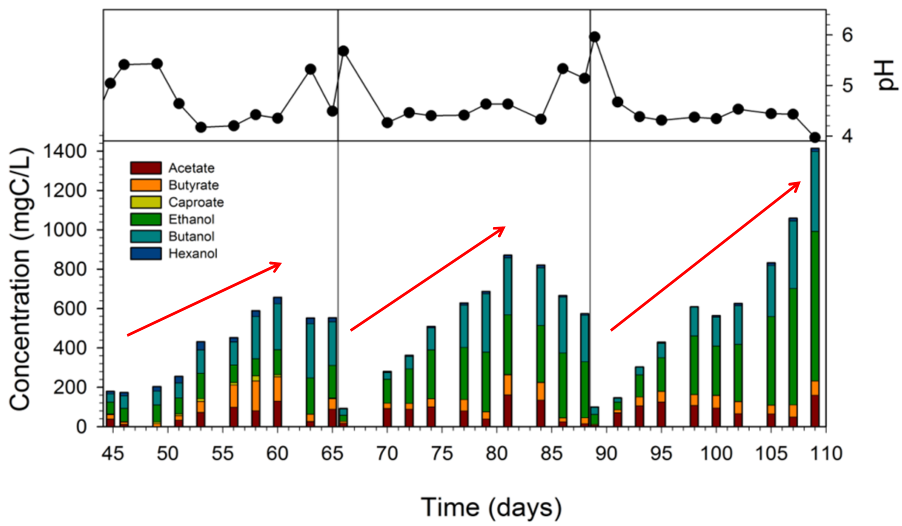

Mikkelsen et al., 2009. *Energ Environ Sci*

# The beginning....Syngas Fermentation




**Total operation period:** 109 d (5 batch)
**Temperature**: 37ºC
**Total reactor volume:** 2L
**Syngas:** 32%$H_2$-32%CO-8%$CO_2$-28%$N_2$
**Syngas injection:** 1 minute every 4 hours

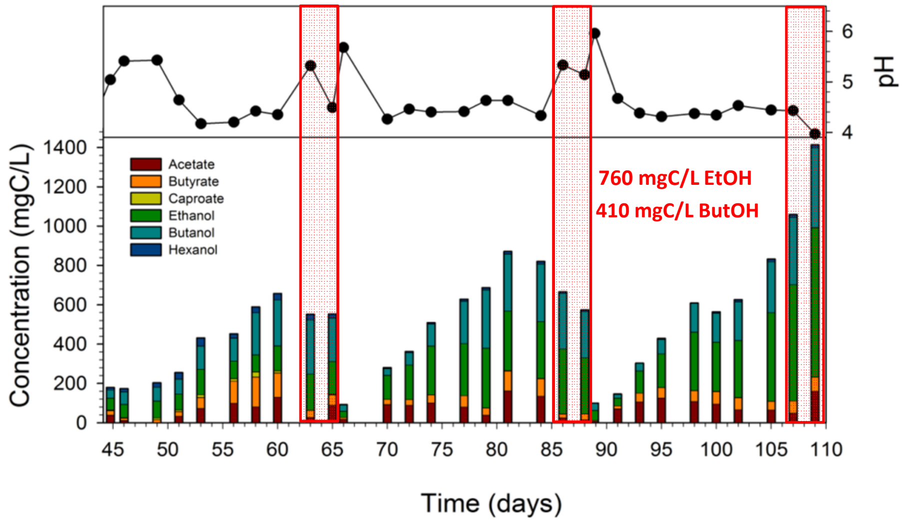
# Syngas Fermentation




*Ganigué et al. LEQUIA. (2016)*

## Syngas Fermentation

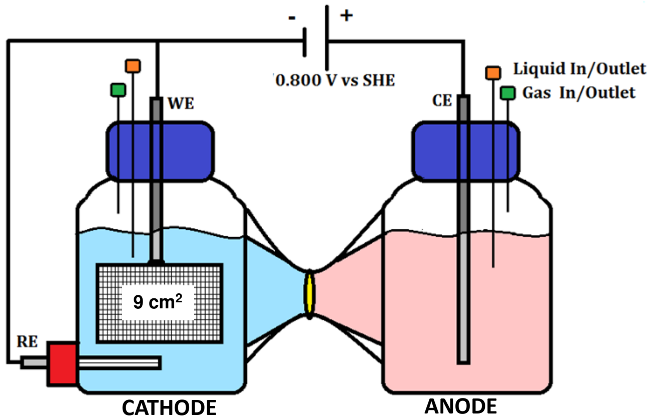
**75%-90% alcohols**




*Ganigué et al. LEQUIA. (2016)*

## Microbial electrosynthesis

**If we managed to do it from syngas, why not in MES?**
(i.e. providing direct reducing power, $e^-$)




**MIXED CULTURE INOCULUM**

# MES of $CH_4$ from $CO_2$

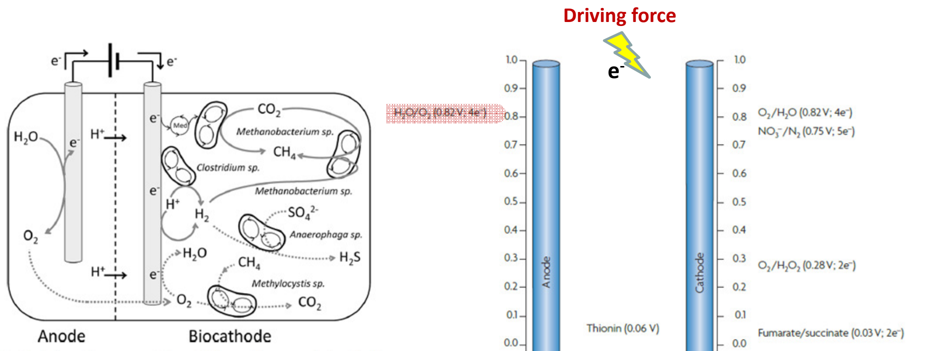



Fig. 4 Schematic representation of the methane producing (solid lines), and cross-over (dashed lines) reactions that took place in the biocathode.

Batlle-Vilanova et al. 2015
RSC Adv., 2015, 5, 52243 Doi:10.1039/c5ra09039c

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# Biomethane

EBA European Biogas Association

What is biomethane?

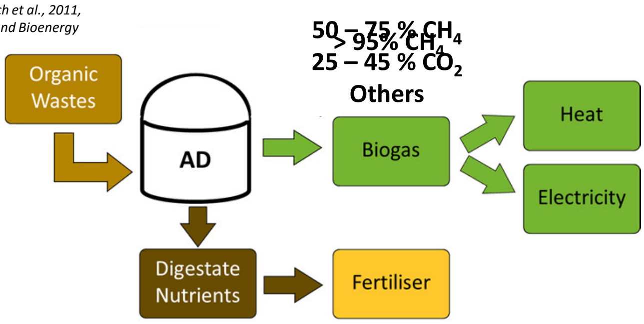
**Upgraded biogas** from Anaerobic digestion

*Source: EBA's BIOMETHANE fact sheet. http://european-biogas.eu/biogas/*

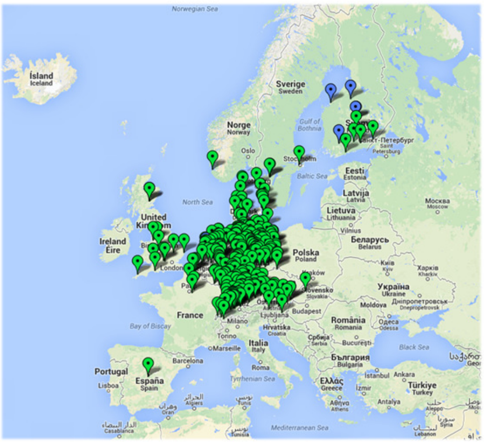
- Removal of harmful trace components
- Increase the calorific value

*Ryckebosch et al., 2011, Biomass and Bioenergy*

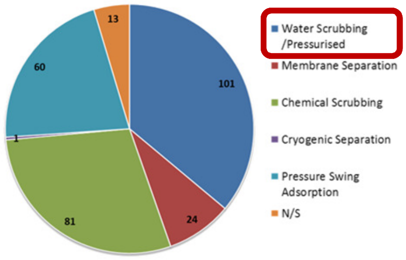
Persson et al., 2006
*IEA Bioenergy, Task 37.*



# Biomethane in the EU

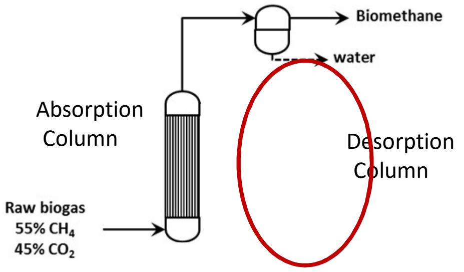


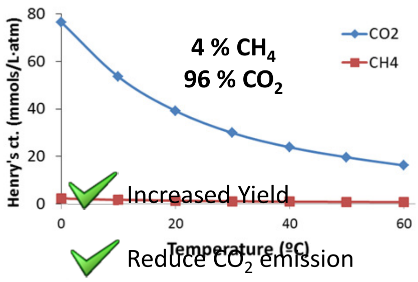

Upgrading and injection, Project map. *Source: Platform biogas partner. http://www.biogaspartner.de/en/project-map.html*




*Source: IEA Bioenergy, Task 37. http://www.iea-biogas.net/plant-list.html (19/08/2014)*

# Biogas upgrading




✗ Energy consumption

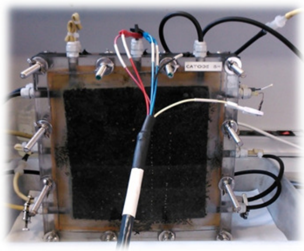
✗ $CO_2$ emission

✓ Increased Yield

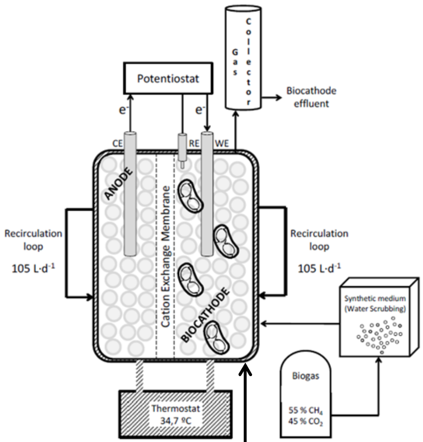
✓ Reduce $CO_2$ emission

**Bioelectrochemical**

**$CO_2$ transformation**



# Materials and methods




**Inoculum from AD**

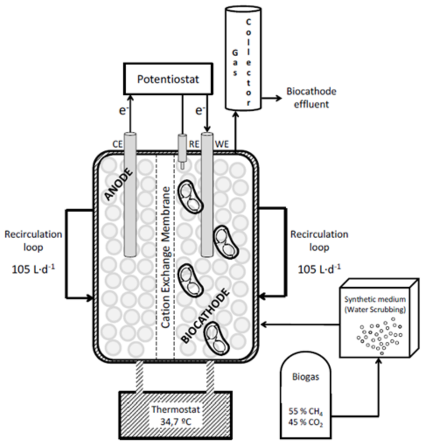
**Biocathode volume** 0,42 L

**Electrode surface** 0,57 $m^2$

**Operation** Batch / Continuous (HRT=18,3h)

**Cathode potential** -800 mV vs SHE


# Materials and methods


**BIOCATHODE**

Electromethanogenesis

$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$  $E'_0$ = -0,24

Hydrogenotrophic methanogenesis

$2H^+ + e^- \rightarrow 4H_2$  $E'_0$ = -0,41

$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$

**ANODE**

Water electrolysis

$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$  $E'_0$ = +0,82

**Thermodynamics**

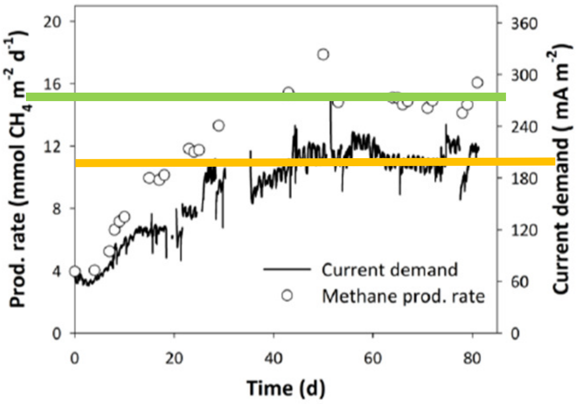
$\Delta G = -n \cdot F \cdot E_{cell}$

$E_{cell} = E_{cat} - E_{an}$

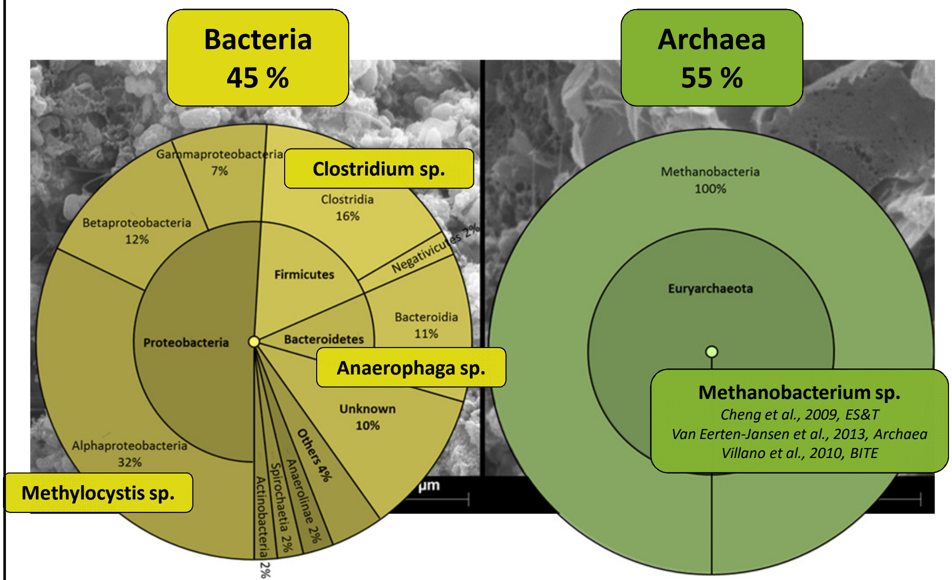
ΔG > 0
Energy required

# Results – Continuous operation

| Current demand (A $m_{NCC}^{-3}$) | pH | Prod rate (mM C $d^{-1}$) | CE (%) |
|---|---|---|---|
| 201.7 ± 18.1 | 7.1 ± 0.2 | 15.4 ± 0.0 | 68.9 ± 0.8 |




# Results – Microbial community



# Results – Microbial community

**BIOCATHODE**

Hydrogenotrophic methanogenesis

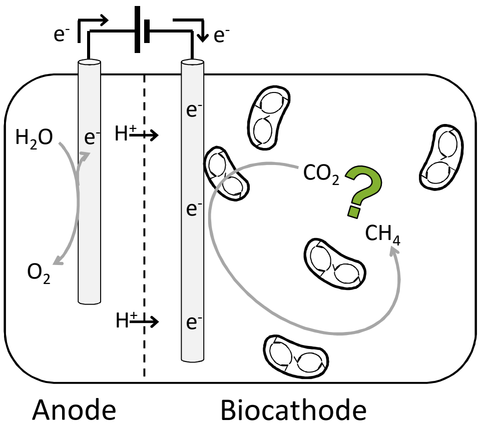
$2H^+ + e^- \rightarrow 4H_2$ E'$_0$ = -0,41 ?

$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$

Electromethanogenesis ?

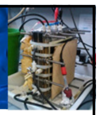
$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$

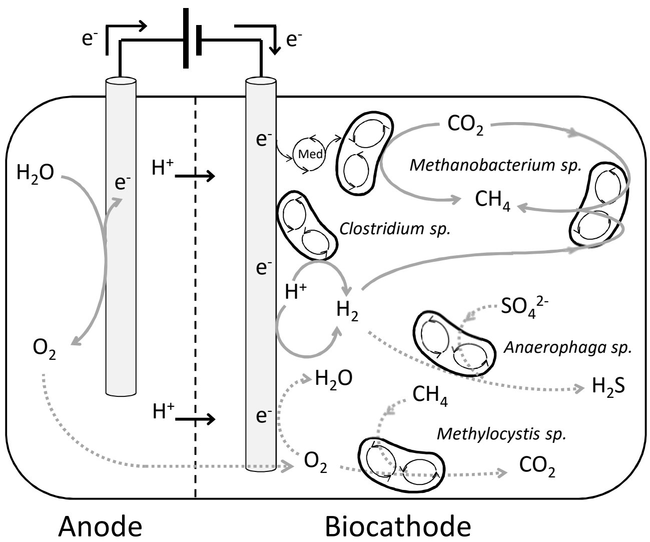
E'$_0$ = -0,24




**Electrochemical characterisation**

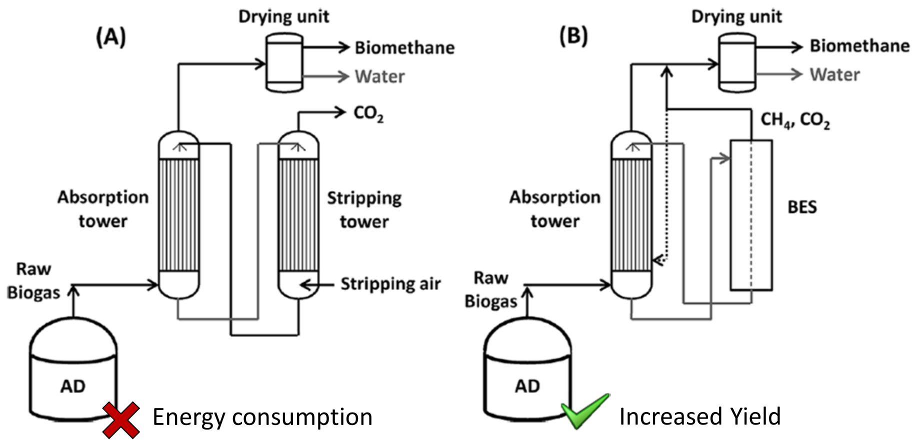
# Results – Methane production mechanism





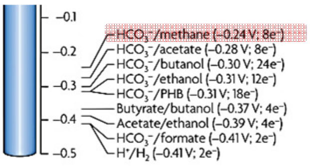

Batlle-Vilanova et al., 2015, RSC Advances

# Perspectives




- ✗ Energy consumption
- ✗ $CO_2$ emission
- ✓ Increased Yield
- ✓ Reduce $CO_2$ emission

# Other products beyond $CH_4$? Acetate…




**Operational conditions drive final product obtained**

*Batlle-Vilanova et al., 2015*
*JCTB, DOI:10.1002/jctb.4657*

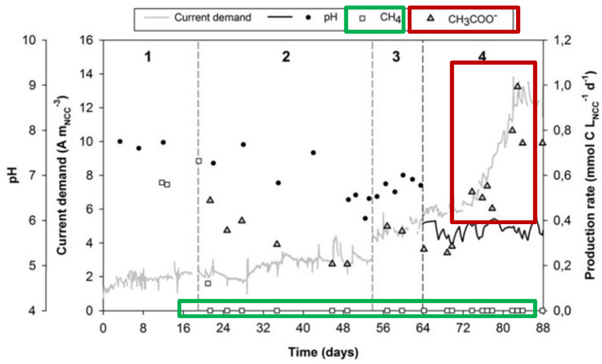



**Figure 2.** Current demand, pH and production rate of methane and acetate during microbial electrosynthesis. The periods are identified in the upper part of the graph according to the applied operational parameters already shown in Table 1. Dashed lines indicate the beginning of each period.

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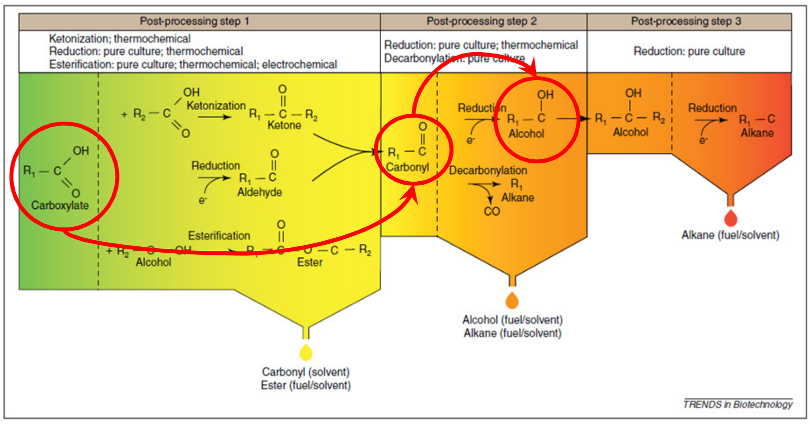
# Other products?

**And from Acetate to ……. Carboxyl pathway**

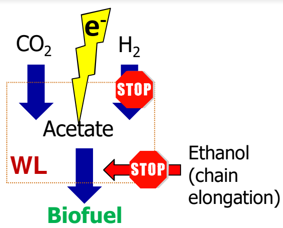



Agler et al. (2011)
Trends in Biotechnology, Vol. 29, No. 2

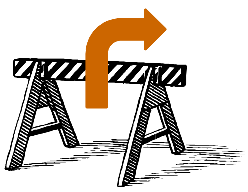
# $CO_2$: Biologic transformation

**Challenges** to overcome:

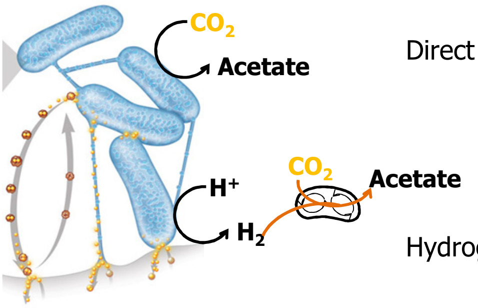
- Limited $H_2$ availability (reducing power).
- Low solubility of $CO_2$ and $H_2$.
- Diverse metabolic routes and products (acids).
- Chemicals needed (ethanol) for carbon chain reactions.




**BioElectroCarbon recycling**



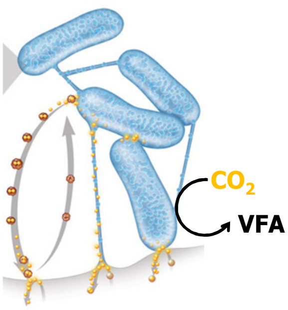
## Mechanisms: DET vs $H_2$-mediated MES ?




Direct Electron Transfer (DET)

Hydrogen-mediated Transfer

## Mechanisms: DET



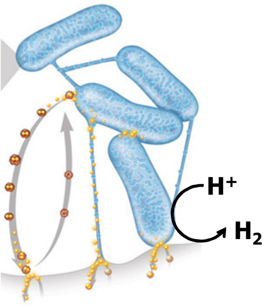

Nevin and co-wokers investigated the capacity of several acetogenic microorganisms (-0.4V vs SHE).

- *Sporomusa ovata* reduced $CO_2$ to acetate (<1 micromole) and small amounts of 2-oxobutyrate.
- Similar results using *Clostridium ljungdhalii, Clostridium aceticum*, but not *Acetobacterium woodii*.

*Nevin et al. (2012) App. & Environ. Microbiol.*

# Mechanisms: $H_2$-mediated Transfer

Abiotic vs. **Biotic** mediated $H_2$ production



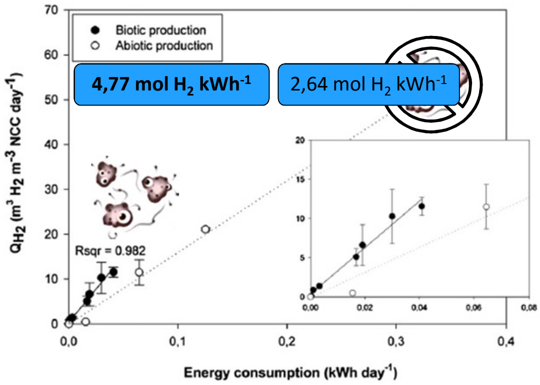




**Fig. 2 – Hydrogen production rate versus energy consumed (linear regression fitted) in the biotic and abiotic MEC.**

*Batlle-Vilanova et al. LEQUIA. (2014) Int. J.of Hydrogen Energy*

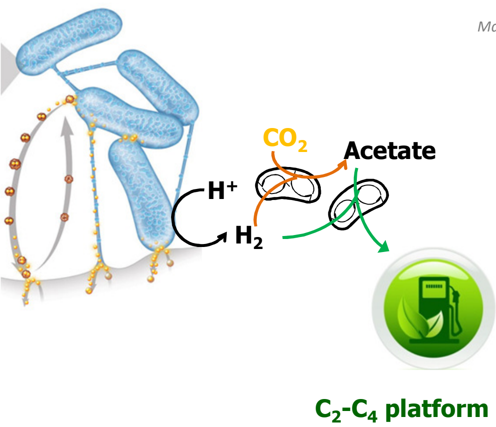
# Mechanisms: $H_2$-mediated Transfer

In the majority of the cases, **acetate** was the main product of bioelectrosynthesis

*Marshal et al. (2012) AEM; Batlle-Vilanova et al. LEQUIA. (2014) JCTB., Patil et al (2015) ES&T, Among others*

At high rates and concentrations.
Even with, *in-situ* electromigration & esterification

*Andersen et al (2014) ES&T*




# Thermodynamics analyses

**Table 1. Secondary fermentation reactions and processes**[a]

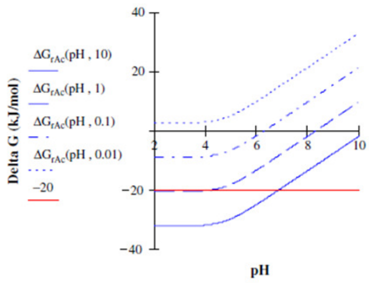
| Reaction | Microbe | Carboxylate conversion reactions | Coupled repetitions[d] | $\Delta G_r^{o'}$ (kJ/mol at 37 °C)[e] | $\Delta G_r^{o'}$ (kJ/mol at 55 °C)[e] |
|---|---|---|---|---|---|
| (c) Carbon dioxide reduction to acetate | *Acetobacterium woodii* | $4H_2 + 2CO_2 \rightarrow$ acetate$^- + H^+ + 2H_2O$ | | −86.78 | −74.56 |
| (d) Hydrogenotrophic methanogenesis | *Methanospirillum hungatei* | $4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$ | | −125.84 | −118.47 |
| (e) Carboxylate reduction with molecular hydrogen | [b] Mixed cultures | acetate$^- + H^+ + 2H_2 \rightarrow$ ethanol $+ H_2O$<br>propionate$^- + H^+ + 2H_2 \rightarrow$ propanol $+ H_2O$<br>*n*-butyrate$^- + H^+ + 2H_2 \rightarrow$ *n*-butanol $+ H_2O$<br>*n*-caproate$^- + H^+ + 2H_2 \rightarrow$ *n*-hexanol $+ H_2O$ | | −7.22<br>−7.49<br>−3.58<br>−7.55 | −4.37<br>−4.59<br>−0.73<br>−3.63 |
| (e) Propionate reduction with ethanol | [c] | ethanol $+ H_2O \rightarrow$ acetate$^- + H^+ + 2H_2$<br>propionate$^- + H^+ + 2H_2 \rightarrow$ propanol $+ H_2O$ | ×1<br>×1 | 7.22<br>−7.49<br>Total = −0.27 | 4.37<br>−4.59<br>Total = −0.22 |
| (f) Aceticlastic methanogenesis | *Methanosaeta soehngenii* | acetate$^- + H^+ \rightarrow CH_4 + CO_2$ | | −39.06 | −43.91 |
| (g) Chain elongation of acetate | *Clostridium kluyveri* | ethanol $+ H_2O \rightarrow$ acetate$^- + H^+ + 2H_2$<br>ethanol + acetate$^- \rightarrow$ *n*-butyrate$^- + H_2O$ | ×1<br>×5 | 7.22<br>−201.68<br>Total = −194.46 | 4.37<br>−198.50<br>Total = −194.13 |
| (g) Chain elongation of *n*-butyrate | *C. kluyveri* | ethanol $+ H_2O \rightarrow$ acetate$^- + H^+ + 2H_2$<br>ethanol + *n*-butyrate$^- \rightarrow$ *n*-caproate$^- + H_2O$ | ×1<br>×5 | 7.22<br>−190.00<br>Total = −182.78 | 4.37<br>−195.20<br>Total = −190.83 |
| (i) Lactate oxidation to *n*-butyrate | *Clostridium acetobutylicum* | 2 acetate$^- + H^+ + 2H_2 \rightarrow$ *n*-butyrate$^- + 2H_2O$<br>2 lactate$^- + H^+ \rightarrow$ *n*-butyrate$^- + 2CO_2 + 2H_2$ | ×1<br>×2.5 | −47.55<br>−209.35<br>Total = −256.90 | −44.10<br>−232.55<br>Total = −276.65 |
| (j) Lactate reduction to propionate | *Selenomonas ruminantium* | lactate$^- + H_2O \rightarrow$ acetate$^- + CO_2 + 2H_2$<br>lactate$^- + H_2 \rightarrow$ propionate$^- + H_2O$ | ×1<br>×2 | 28.51<br>−86.63<br>Total = −58.12 | 25.96<br>−85.21<br>Total = −59.25 |

[a]Secondary fermentation reactions correspond to those in Figure 1 [(h) is not shown here].
[b]Carboxylate reduction to alcohol with $H_2$ as the electron donor has been observed in undefined mixed cultures [23].

*Agler et al. (2011). Trends in Biotechnology*

# Thermodynamics analyses


$$\Delta G_r' = \Delta G_r^0 + RT \ln \frac{[\text{Alcohol}]}{[\text{VFA}_t] pH_2^2} + RT \ln \frac{K_a + [H^+]}{K_a [H^+]}$$




**Low pH**

**High $P_{H2}$**

minimal reaction energy for maintenance and growth

**Fig. 2 – Gibbs free energy change of bio reduction of acetic acid as function of pH at different $H_2$ partial pressure of 0.01 bar (········), 0.1 bar (-·-·-·), 1 bar (- - - -) and 10 bar (——) at 1 M acetic acid (sum of dissociated and undissociated) and ethanol and the thermodynamic limit of −20 kJ/mol (——).**

*Steinbusch et al. (2008) Water Research*

# $C_2$-$C_4$ platform chemicals

## The magic treble

1. **Carbon Source** ($CO_2$)
2. Reducing power ($H_2$). **High $P_{H2}$**
3. **Carboxydotrophic mixed culture**

From AD enrichment with syngas ...

| DGGE band | Closest Bacterial species | Identities (%) |
|---|---|---|
| *1* | *Clostridium carboxidivorans* P7 (NR_104768.1)<br>*Clostridium scatologenes* K29 (AB610570)<br>*Clostridium drakei* FP (NR_114863.1) | 100 |
| *2* | *Clostridium ljungdahlii* DSM13528 (NR_074161.1)<br>*Clostridium ragsdalei* (DQ020022)<br>*Clostridium autoethanogenum* DSM10061 (CP006763.1) | 100 |
| 3 | Uncultured *Firmicutes* clone (GU559846.1) | 94 |

*Ganigué et al. LEQUIA. (2015) Chem. Commun.*

# $C_4$ Organic acids – Proof of concept

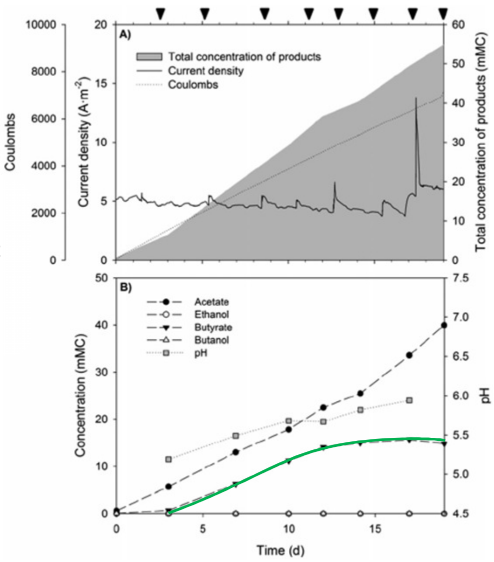
**Inoculum sources:** Syngas fermentor
**Cathode potential:** -0,8 V vs SHE
**Batch operation**
**Methanogenesis inhibitor**

Stable current density **5 A m$^{-2}$**

Total concentration of products **55 mM C**

$CO_2$ conversion rate **2,9 mMC d$^{-1}$**

Butyrate production rate **1,49 mMC d$^{-1}$**

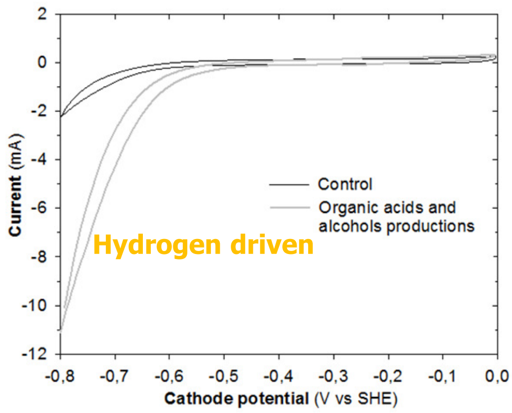



*Ganigué et al. LEQUIA. (2015) Chem. Commun.*

# $C_4$ Organic acids – Proof of concept

**Inoculum sources:** Syngas fermentor
**Cathode potential:** -0,8 V vs SHE
**Batch operation**
**Methanogenesis inhibitor**

**Electrochemical characterization**



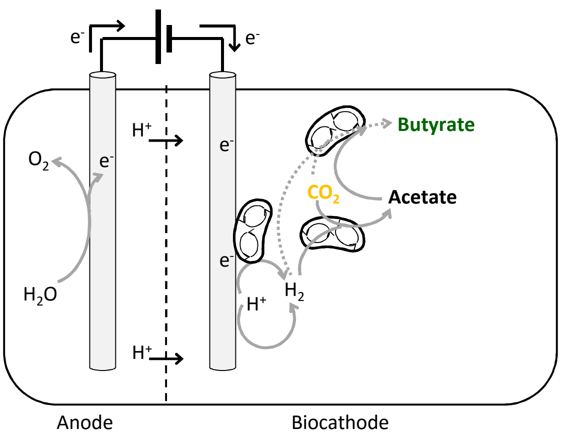

*Ganigué et al. LEQUIA. (2015) Chem. Commun.*

# $C_4$ Organic acids – Proof of concept

**Inoculum sources:** Syngas fermentor
**Cathode potential:** -0,8 V vs SHE
**Batch operation**
**Methanogenesis inhibitor**

***Clostridium carboxidivorans/ Clostridium ragsdalei*:**

Wood-Ljungdahl + Acetyl-CoA reduction

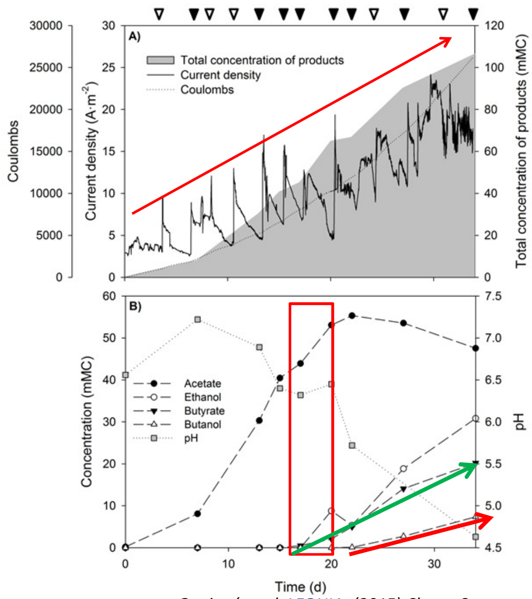



Ganigué et al., 2015. *Chem Comm*
Agler et al., 2011. *Trends Biotechnol*
Daniell and Köpke, 2012. *Energies*
Thauer et al., 1977. *Bacteriol Reviews*

# $C_4$ Alcohols– Proof of concept

**Inoculum sources:** Syngas fermentor
**Cathode potential:** -0,8 V vs SHE
**Batch operation**
**Methanogenesis inhibitor**

**1st Proof of concept: Bioalcohols production**



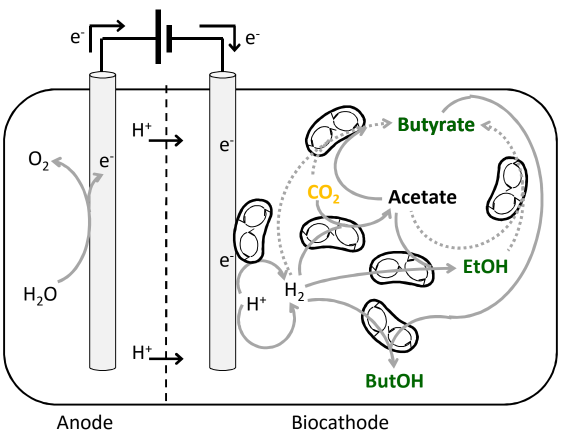

*Ganigué et al.* LEQUIA. *(2015) Chem. Commun.*

# $C_4$ Alcohols– Proof of concept

**Inoculum sources:** Syngas fermentor
**Cathode potential:** -0,8 V vs SHE
**Batch operation**
**Methanogenesis inhibitor**

***Clostridium kluyveri*:**

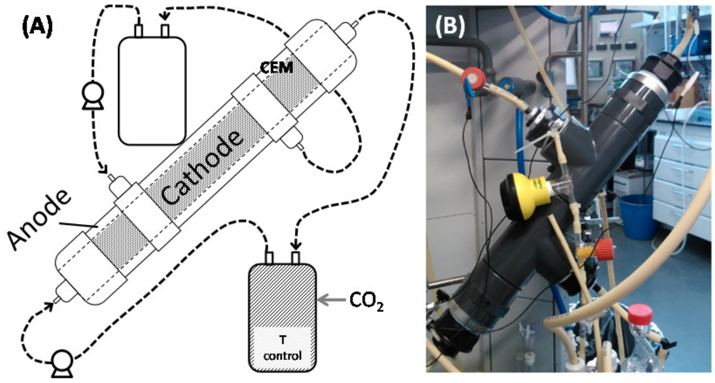
Chain elongation (acetate + ethanol)




Ganigué et al., 2015. *Chem Comm*
Agler et al., 2011. *Trends Biotechnol*
Daniell and Köpke, 2012. *Energies*
Thauer et al., 1977. *Bacteriol Reviews*

## $C_4$ Organic acids– towards selective production

**Inoculum sources:** Syngas fermentor
**Cathode potential:** -0,8 V vs SHE
**Batch operation**

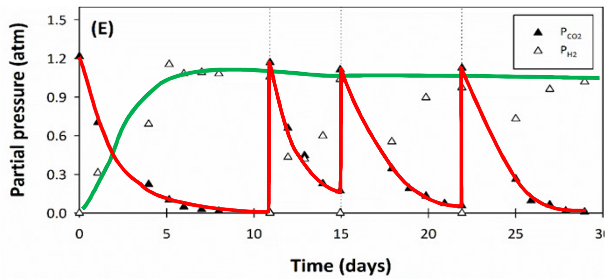



*Batlle-Vilanova et al.* LEQUIA. *(2016)*

## $C_4$ Organic acids– towards selective production

**Inoculum sources:** Syngas fermentor
**Cathode potential:** -0,8 V vs SHE
**Batch operation**

**Increase $P_{H2}$**



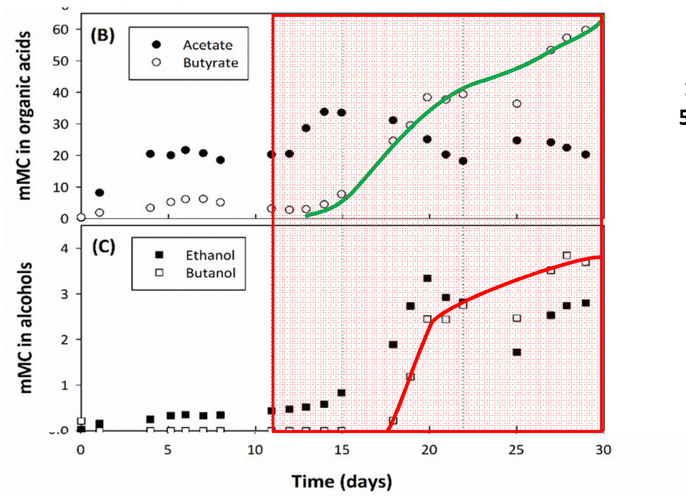

74

*Batlle-Vilanova et al.* LEQUIA. *(in preparation)*

## $C_4$ Organic acids– towards selective production

**Inoculum sources:** Syngas fermentor
**Cathode potential:** -0,8 V vs SHE
**Batch operation**

**Selective production of:**
- Butyrate vs Acetate
- Acids vs Alcohols




**17.0 mM C-Acetate**
**50.8 mM C-Butyrate**

**Ratio Buty/Ac = 3**

*Batlle-Vilanova et al. LEQUIA (in preparation)*

## $C_4$ Organic acids– extraction of the final product

### Selective separation of Butyrate

Impregnated Hollow fibre membrane: 3M-S6/2
$Ø_{in}$= 180 µm; $Ø_{ext}$ = 980 µm
Porous: 0,2 µm

Impregnated with:
dodecane/dodecanol (6%, v/v)

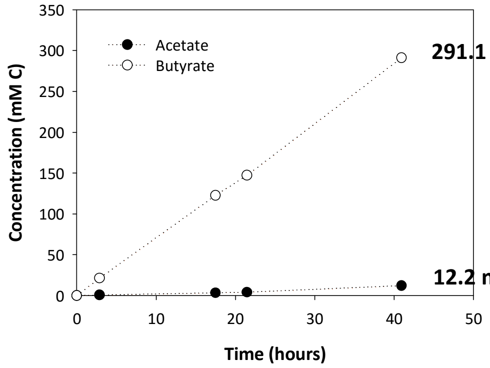
Extracting phase: NaOH, 0.1M

**Initial solution**

**17.0 mM C-Acetate**
**50.8 mM C-Butyrate**
**Ratio But/Ac = 3**

## $C_4$ Organic acids– extraction of the final product

### Selective separation of Butyrate




**291.1 mM C-Butyrate**

**Ratio But/Ac = 24**

**12.2 mM C-Acetate**

**Initial solution**

17.0 mM C-Acetate
50.8 mM C-Butyrate
**Ratio But/Ac = 3**

x8

**Final (40 hours)**

12.2mM C-Acetate
291 mM C-Butyrate
**Ratio But/Ac = 24**

# MFC: Swine manure treatment

**Farm**

Swine manure influent

High **organic matter** and **ammonium** content

**MFC**

Swine manure effluent

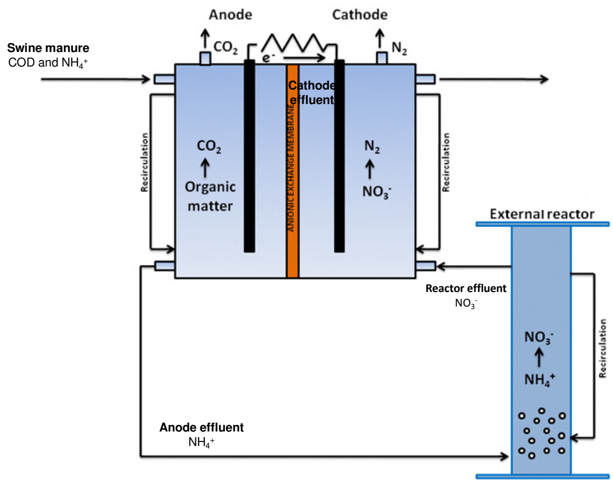
Low **organic matter** and **nitrate**
No **ammonium**

MFC characteristics

MFC dimensions:
1,21x0,71x1,36m
Reactor dimensions:
1,50x0,20m

Flow: 50 L·day$^{-1}$
HRT: 30 hours

# Design




Based on Virdis *et al.*, 2008

**Vilajeliu-Pons** et al., LEQUIA (2015), *HAZMAT*

## Design

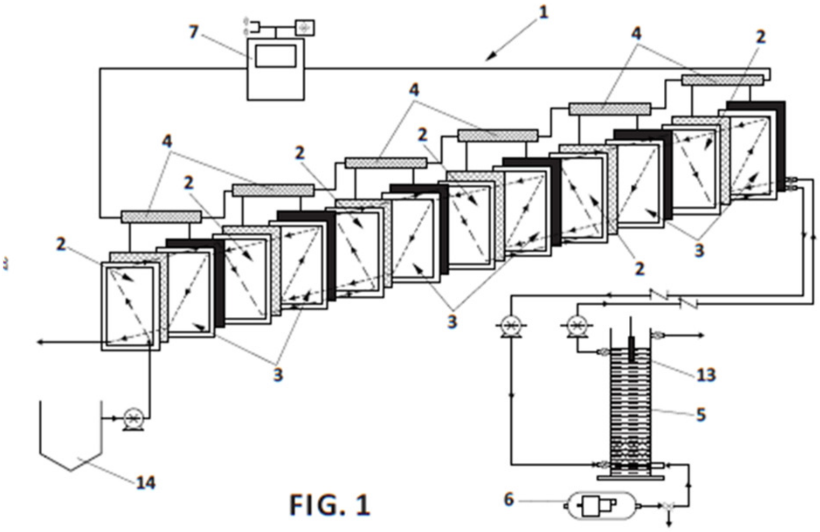



FIG. 1

**Patent Abengoa Water & LEQUIA**

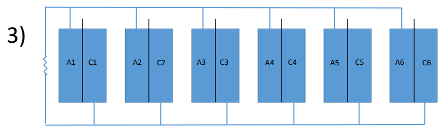
## Materials

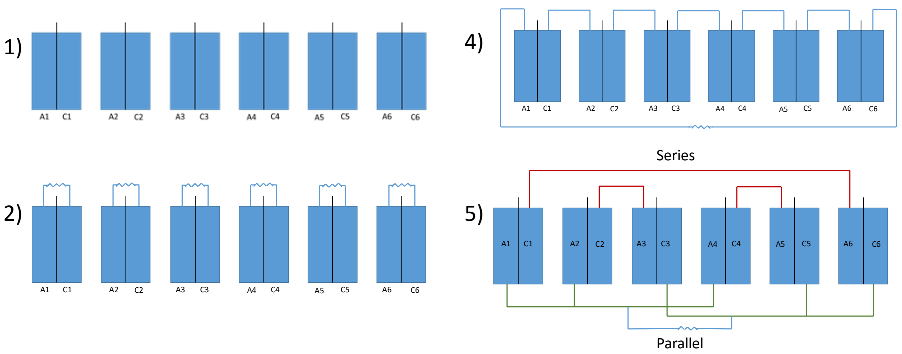
Granular graphite

Stainless steel
mesh

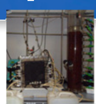
# Electrical configurations

1) OCV
2) Individual
3) Parallel
4) Series
5) Mix (series-parallel)




# Different scale-MFC comparison



| Process | Analysed parameter | mL-SCALE | [illegible] | [illegible] |
|---|---|---|---|---|
| Operational | Net volume | 6 | [illegible] | [illegible] |
| | Flow | 3 | [illegible] | [illegible] |
| Organic matter oxidation | Organic matter removal rate | 2.09±0.76 | 1.65±1.00 | kg COD m$^{-3}$ d$^{-1}$ |
| | Organic matter removal efficiency | 15 | [illegible] | % |
| | Coulombic efficiency | 24 | [illegible] | % |
| Nitrification | Nitrification rate | 0.26±0.06 | 0.34±0.10 | kg N m$^{-3}$ d$^{-1}$ |
| | Nitrification efficiency | <92 | <92 | % |
| Denitrification | Nitrogen removal rate | 0.16±0.06 | 0.13±0.08 | kg N m$^{-3}$ d$^{-1}$ |
| | Nitrogen removal efficiency | 7 | [illegible] | [illegible] |
| | Coulombic efficiency | 10 | [illegible] | % |
| Electricity production | Power density | 20 | 300 | mW m$^{-3}$ |

High treatment efficiency with low CE

Similar workability

Higher power density recovered

# Nitrate contamination

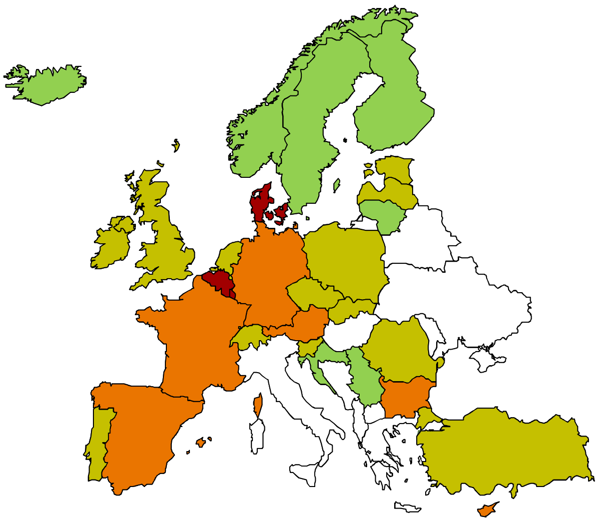
EEA

Percentage of wells with safe levels of nitrates ($<25$ ppm $NO_3^-$)

- >95%
- 75% < X < 95%
- 50% < X < 75%
- 25% < X < 50%
- No data

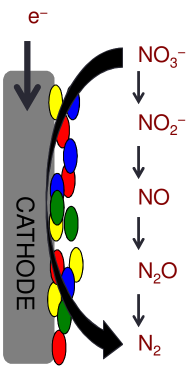
World Health Organization

Guideline WHO: 50 ppm$NO_3^-$ (11.29 ppmN-$NO_3^-$)



European Environment Agency, 2009.

# dBES. Background



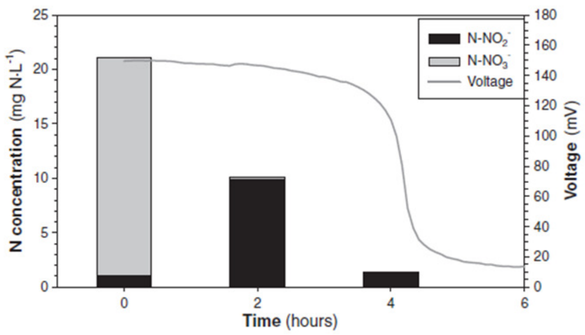
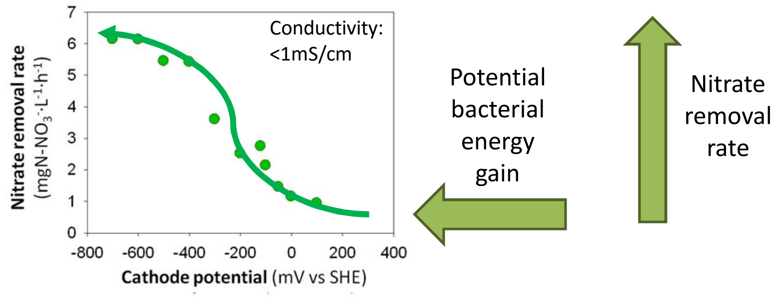




Fig. 2. Relationship between nitrogen compound dynamics and voltage in the denitrifying cathode MFC.

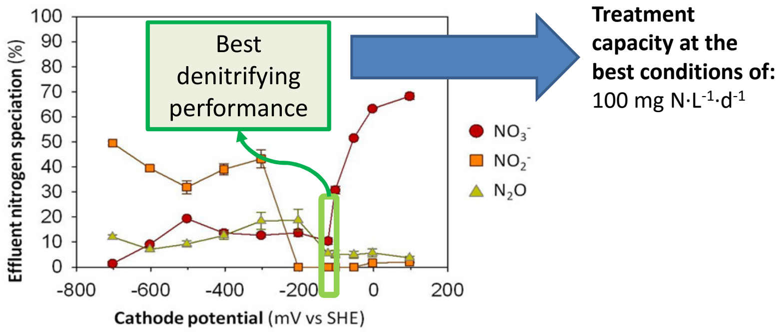
**Clauwaert** et al. 2007, *Env. Sci. &Technol*
**Puig** et al. 2012, *Env. Sci. &Technol.* 46 (4), 2309.

# Cathode potential in groundwater treatment




**Pous** et al., (2015), *Chem. Eng. J. 263, 151-159*

# Cathode potential in groundwater treatment

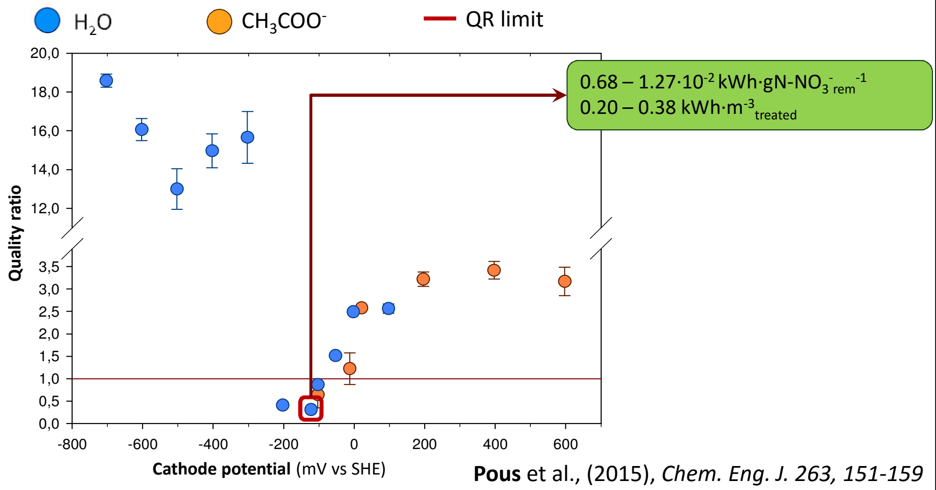



**Pous** et al., (2015), *Chem. Eng. J. 263, 151-159*

# Cathode potential in groundwater treatment

World Health Organization

$QR = [NO_3^-] / 11.29 + [NO_2^-] / 0.91 \leq 1$




**Pous** et al., (2015), *Chem. Eng. J. 263, 151-159*


# Cathode potential in groundwater treatment

World Health Organization

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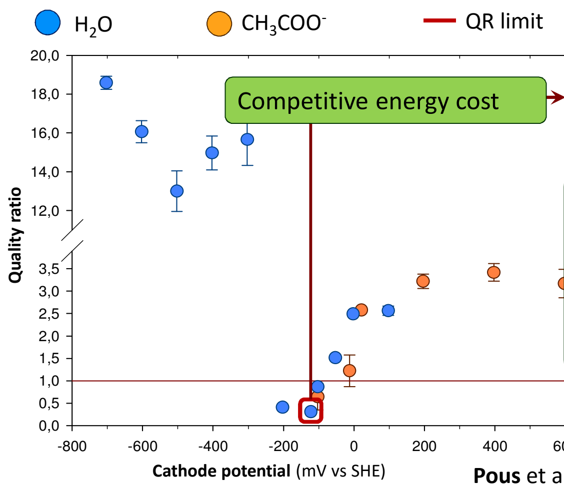
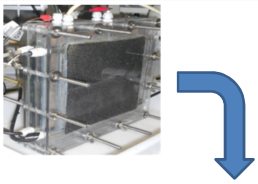
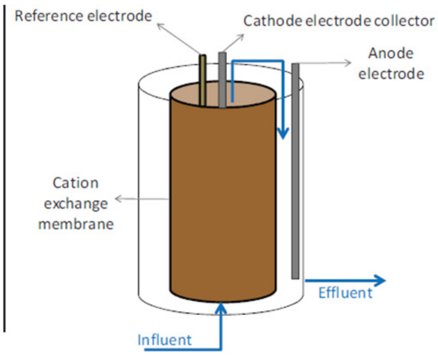



- Reverse electrodialysis
  - $0.40 – 4.95 \cdot 10^{-2}$ kWh·gN-$NO_3^-{}_{rem}^{-1}$
  - $0.04 – 1.69$ kWh·$m^{-3}_{treated}$
  - (El Midaoui et al., 2002; Ortiz et al., 2008; Twomey et al., 2010)
- Reverse osmosis
  - $1.03 – 2.09$ kWh·$m^{-3}_{treated}$
  - (Twomey et al., 2010)

**Pous** et al., (2015), *Chem. Eng. J. 263, 151-159*

## Water application





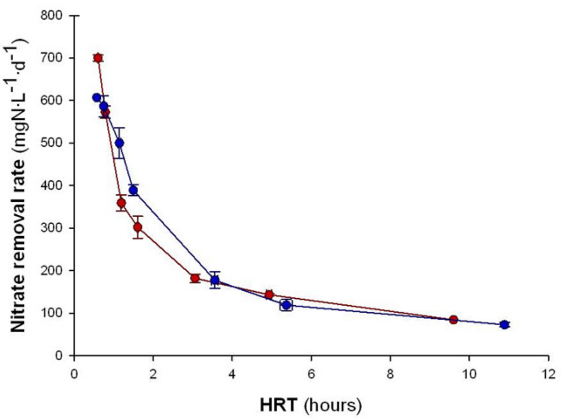

## Water application

**Anode potential: > + 800 mV vs SHE**

| Electron donor | Oxidation reaction (redox potential at pH 7) | Electrode material | Catalysis |
|---|---|---|---|
| Acetate | E0’ = -290 mV vs SHE | Graphite | Biotic |
| Water | E0’ = +840 mV vs SHE | Graphite | Abiotic |
| | | Stainless steel | Abiotic |
| Chloride | E0’ = +890 mV vs SHE | Ti-MMO | Abiotic |

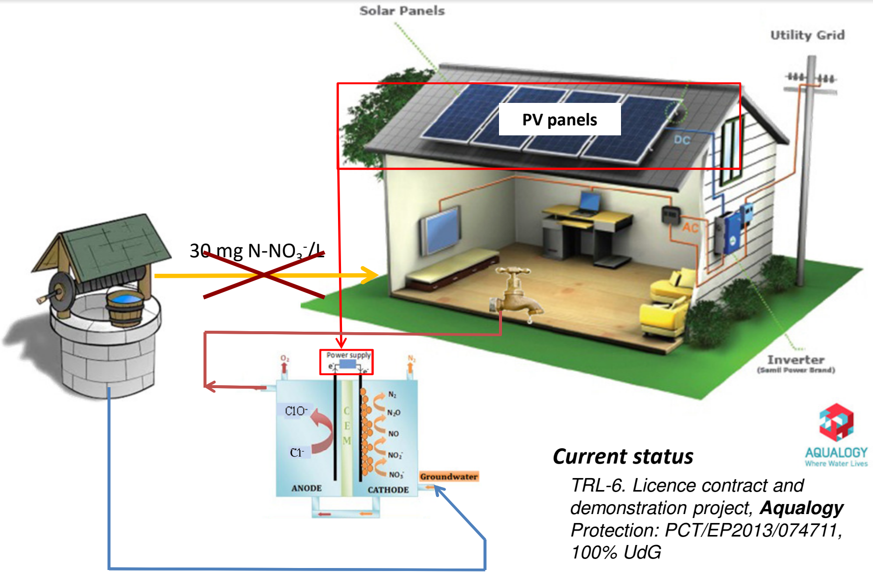
**Nitrogen reduction and desinfection using the same tech!**

# Water application




**European Patent**
**WO 2014082989 A1**

# Water application

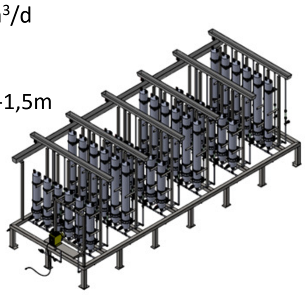



***Current status***

*TRL-6. Licence contract and demonstration project, **Aqualogy***
*Protection: PCT/EP2013/074711, 100% UdG*

# Water application

Flow: 2 $m^3/d$
36 BES
$d_{cat}$: 9cm;
Height: 1-1,5m



***Current status***

*TRL-6. Licence contract and demonstration project,* ***Aqualogy***
*Protection: PCT/EP2013/074711, 100% UdG*

# CFD – LEQUIA

**EXPERIENCE in Biological nutrient removal wastewater applications**

+

**Modelling works to optimize biological performance**

**But...**

**assumptions: Ideal mixing conditions, one phase (or two phase with limiations), ...**

**CFD**

*New reactor designs*

*Multiphase simulations*

*Combination of CFD and biological models*

*Application of CFD within different biological nutrient removal configurations*

## CFD plataform

CFD platforms

ANSYS FLUENT

OPEN FOAM

STAR C++,

simFlow

among others

## CFD – Applications

1) Testing **Microbial Fuel Cells** configurations.

- Hydrodynamic simulation for different anodic cell configurations (different electrode materials)

- Incorporation of biological models

RSC Advances

PAPER

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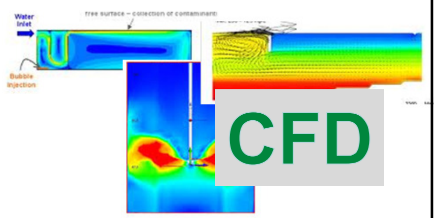
Cite this: RSC Adv., 2015, 5, 78994

**Anode hydrodynamics in bioelectrochemical systems†**

Albert Vilà-Rovira, Sebastià Puig,* M. Dolors Balaguer and Jesús Colprim

# CFD – Objectives?

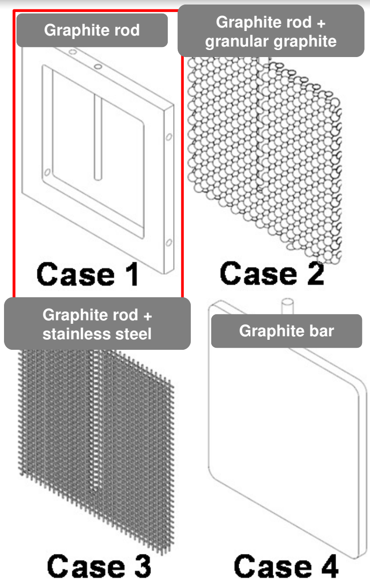
BES OPTIMIZATION




**Key parameters**

- Substrate availability
- Electrode design
- Microbial community

# CFD - Configurations



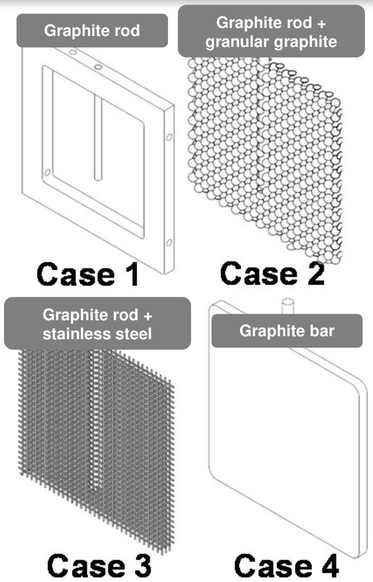

- Graphite rod
- Graphite rod + granular graphite
- Graphite rod + stainless steel mesh
- Graphite bar

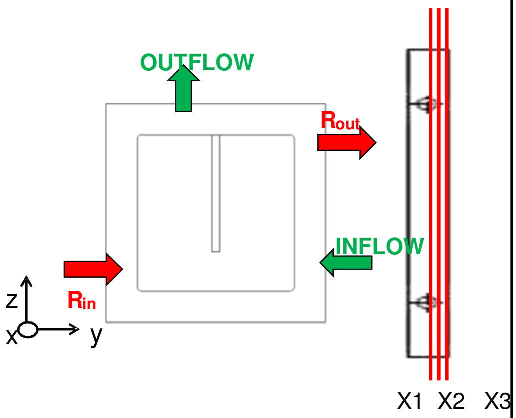
**Integrated in CFD**

Biological model

CFD model development

# CFD - Configurations




# MFC hydrodynamics

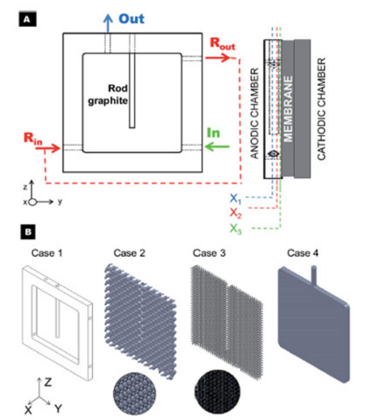
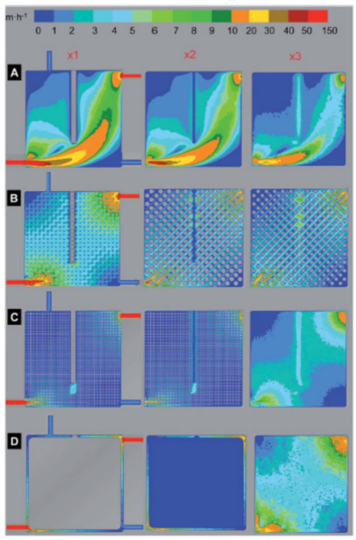
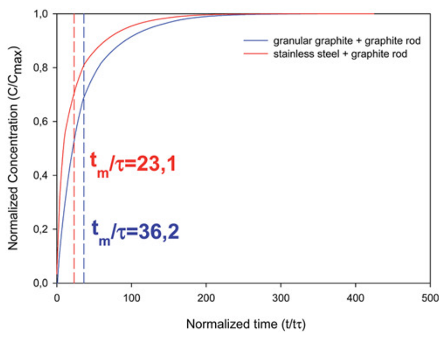
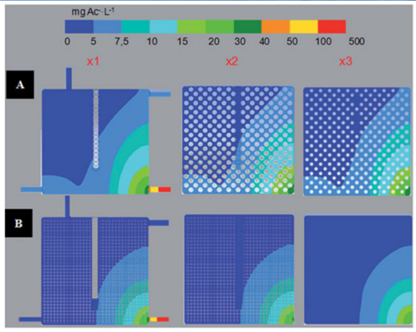



Fig. 1 Representation of the reactor design: (a) reactor flowchart and the selected planes for results plotting ($x_1$, $x_2$ and $x_3$), (b) different electrode materials used: graphite rod (Case 1), granular graphite (Case 2), stainless steel (Case 3) and graphite plate (Case 4). Rin and Rout represented inlet and outlet recirculation's streams, respectively.



# MFC Hydrodynamics

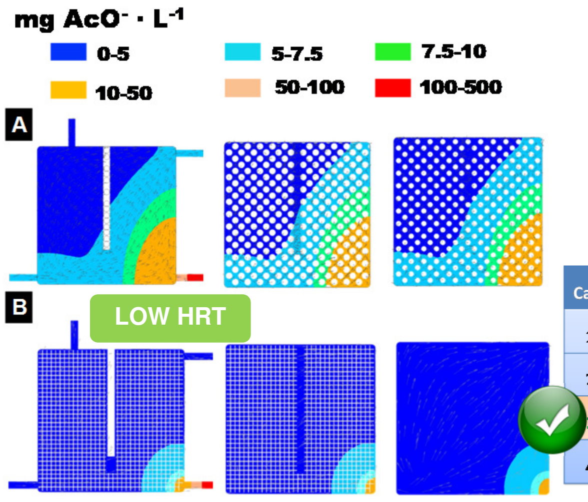



| Case | Electrode material | $m^2$ per $m^3$ NAC | Void fraction | HRT (hours) | Power ($W\ m^{-2}$) | I ($A\ m^{-2}$) | C.E (%) | $CH_4$ prod. (mL per day) |
|---|---|---|---|---|---|---|---|---|
| 1 | Graphite rod | 14.76 | 0.98 | 12 | — | — | — | — |
| 2 | Graphite rod plus granular graphite | 225.44 | 0.75 | 9.55 | 0.02 | 0.40 | 52 | 26.9 |
| 3 | Graphite rod plus stainless steel mesh | 213.81 | 0.94 | 12.08 | 0.14 | 0.36 | 58 | 28.6 |
| 4 | Graphite plate | 208.7 | 0.50 | 6.41 | — | — | — | — |

# MFC – Chemicals evolution

Substrate availability




NO DEATH ZONES

HIGHER REACTION SURFACE

| Case | Anodic surface area ($m^2$) | Power ($W/m^2$) |
|---|---|---|
| 1 | 0.012 | 0.011 |
| 2 | 0.525 | 0.510 |
| 3 | 3.198 | 3.110 |
| 4 | 0.072 | 0.070 |

# CFD – Biological processes

1) Anammox reactor modelling , new design:

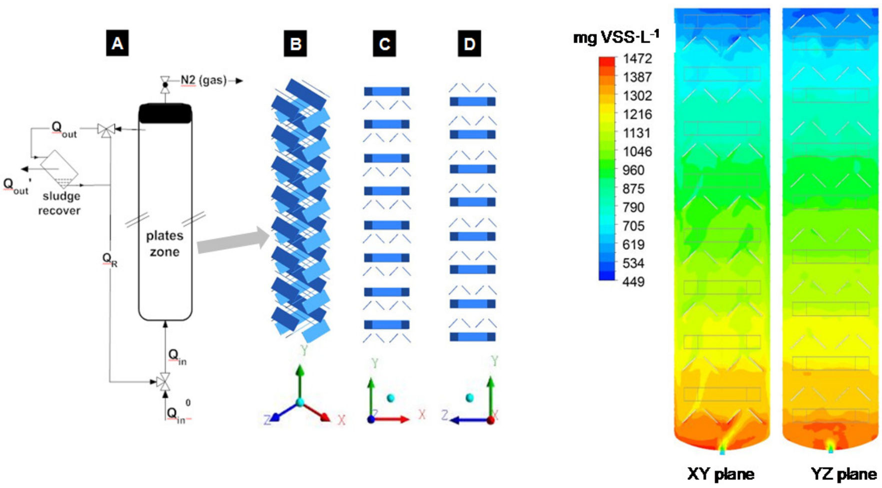
- Introduction of biological models within CFD models

- Multiphase simulations -> account the influence of the generated gas in anammox process within the hydrodynamics

- Addition of a pseudo – solid phase to relate the reaction to the sludge localization inside the reactor.

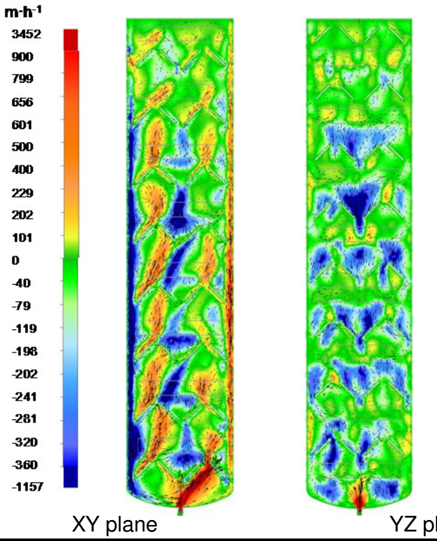
# CFD – Biological processes

**2) Anammox process: hydrodynamic + bio – model for a multjphase process**



# CFD – Biological processes

Upflow velocities



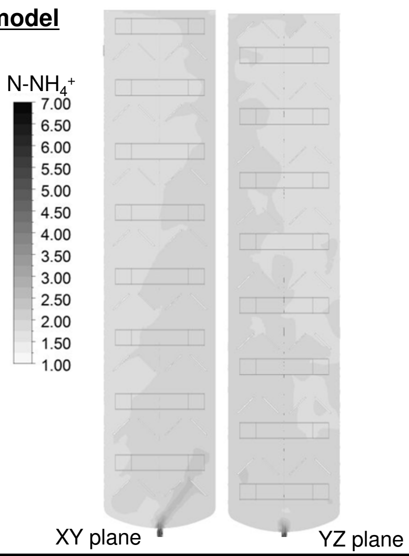

**Velocity vectors**

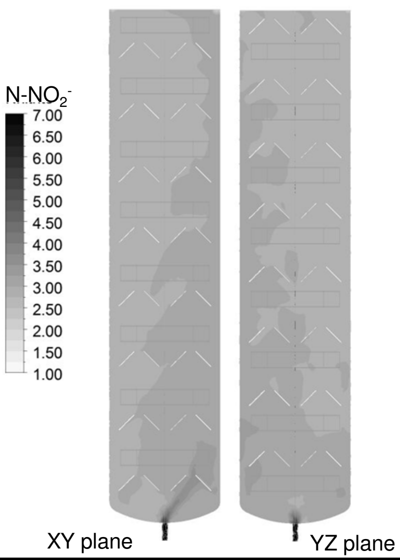
Minimum fluidization velocity: 5 $m \cdot h^{-1}$

Optimal Range of 7 – 8 $m \cdot h^{-1}$ ($\phi_p$ = 500 µm)

# CFD – Biological processes

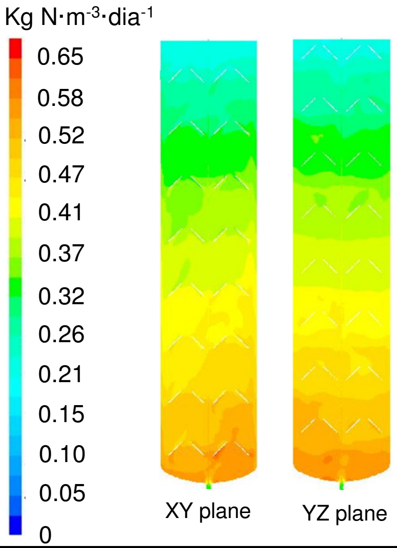
**biomodel**



# CFD – Biological processes

**$N_2$ (gas) production rate**




**Our Team**

lequia ECO-INNOVATIVE WATER SOLUTIONS UdG

TECNIO

Universitat de Girona

Universitat de Girona

# Aplicació de tecnologies bio-electroquímiques al tractament d'aigües

**Gràcies per la vostra atenció**

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