Cátedra FACSA de innovación en el ciclo integral del agua
UNIVERSITAT JAUME•I

Nicho de tecnologías electroquímicas microbianas: de la biorremediación a la electro-fermentación

Sebastià Puig
19 de Abril de 2018

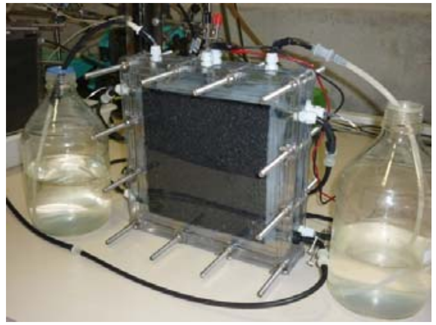
lequia UdG ECO-INNOVATIVE WATER SOLUTIONS

tecnio catalonia Fins a 31/12/2019
ACCIÓ Generalitat de Catalunya

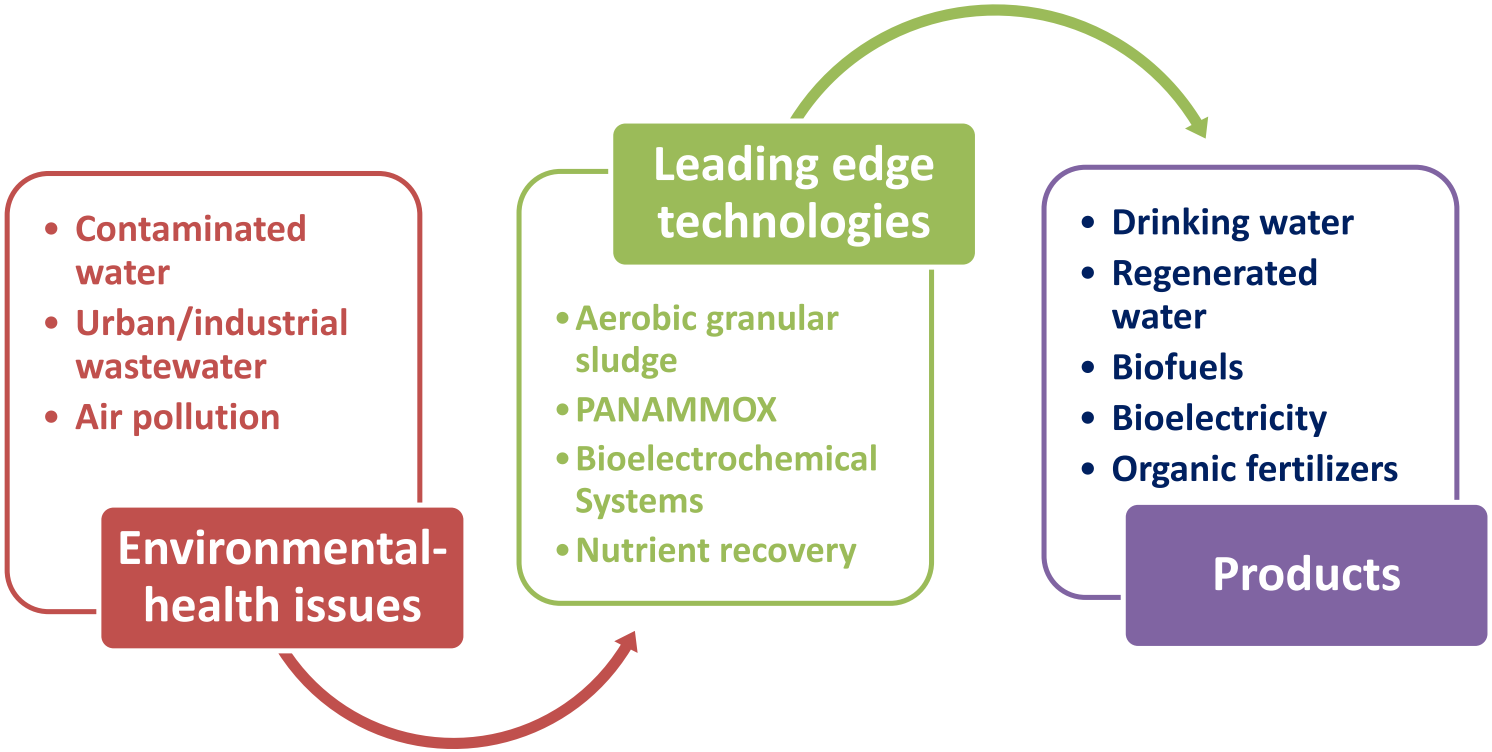
Universitat de Girona

[Team: LEQUiA scientific expertise]

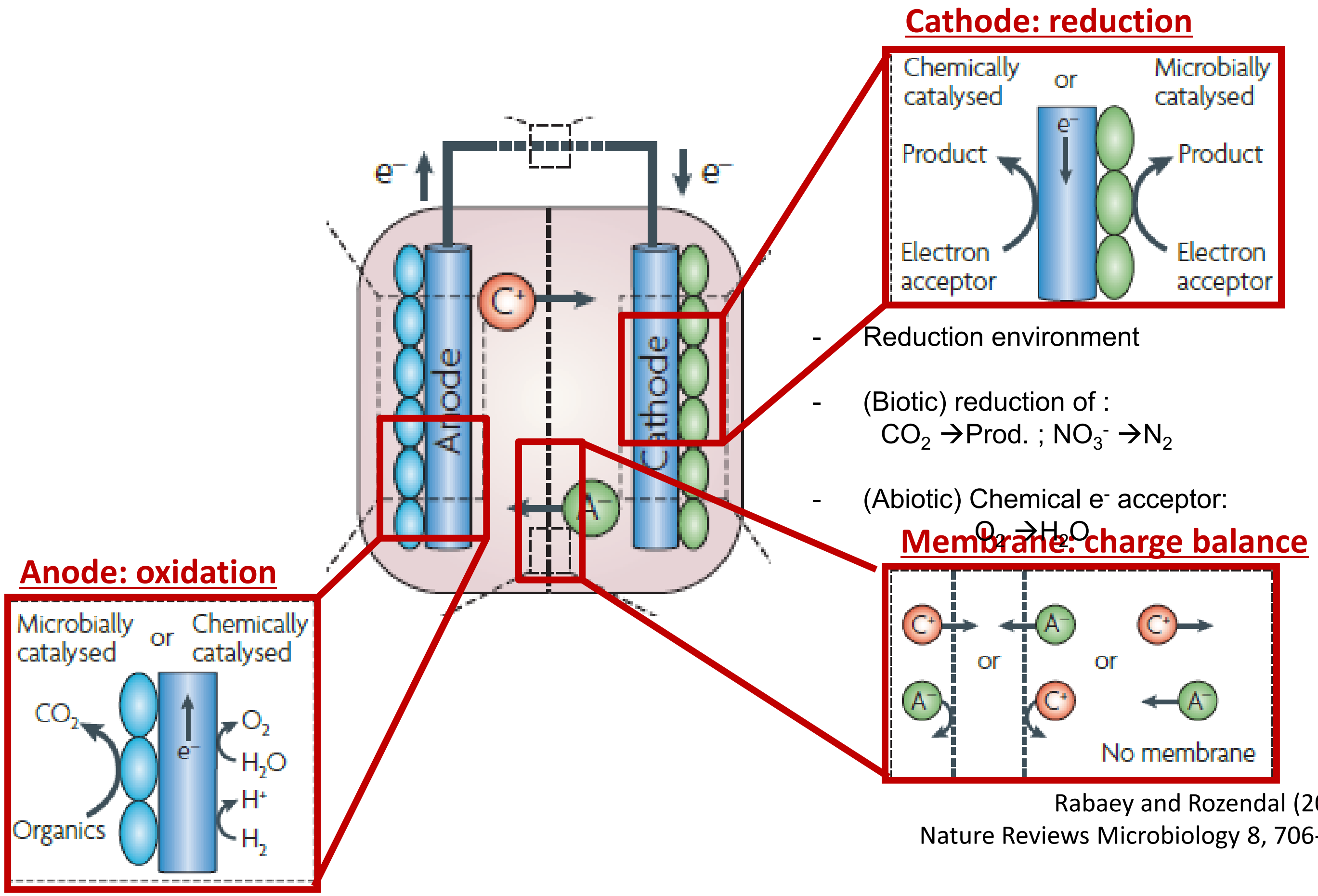
- Biological nutrient removal and recovery from liquid waste
- Bioelectroremediation of polluted water
- CO_2 capture and transformation to C-neutral products (BES)
- Advanced adsorption and oxidation processes for siloxanes, odorous sulphur compounds, VOC.
- Membrane fouling and clogging: from basic research of the responsible parameters to practical aspects for cleaning and monitoring.
- Environmental Decision Support Systems (EDSS) to support decision making in water-related systems.

Group Leader: Dr. Jesús Colprim



Contaminated water
Urban/industrial wastewater
Air pollution
Environmental-health issues
Leading edge technologies
Aerobic granular sludge
PANAMMOX
Bioelectrochemical Systems
Nutrient recovery
Drinking water
Regenerated water
Biofuels
Bioelectricity
Organic fertilizers
Products

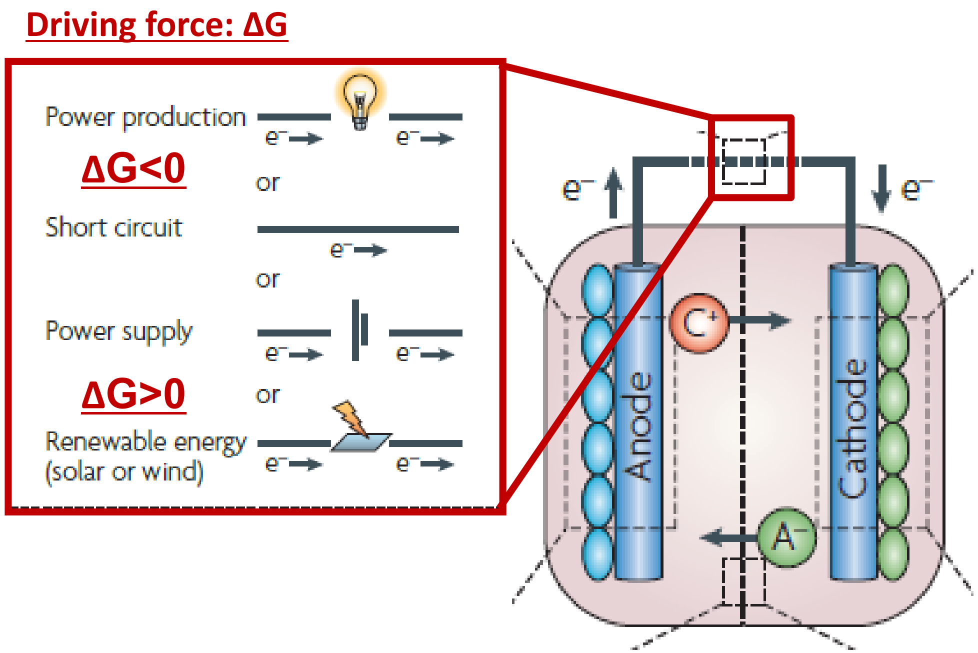


- Reduction environment

- (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

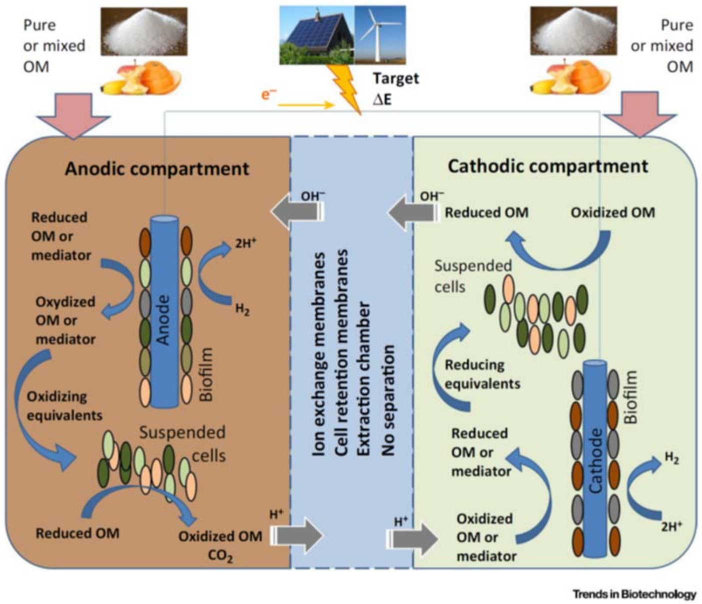


Rabaey and Rozendal (2010)
Nature Reviews Microbiology 8, 706-716

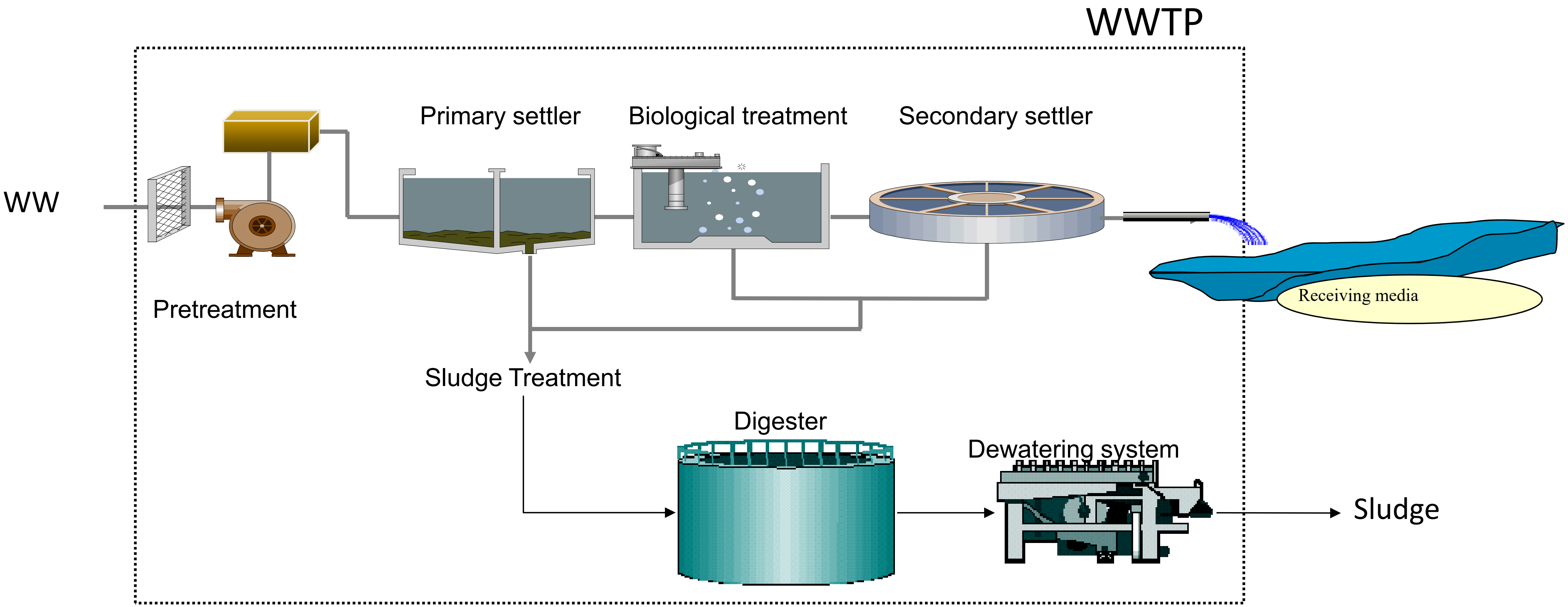
Multiple options!

- focus on anodic reactions: oxidation of chemical compounds
- focus on cathode reactions (**biocathodes**): reduction of chemical compounds
- Direct electron flow (electricity production, spontaneous reactions)
- Forced electron flow (electricity consumption/storage, non spontaneous reactions)

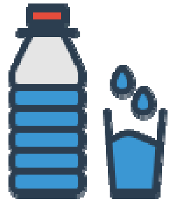
we can fix environmental potential! Use of a potentiostat!



Schievano et al. (2016) LEQUIA Trends in Biotechnology


WWTP
WW
Pretreatment
Primary settler
Biological treatment
Secondary settler
Receiving media
Sludge Treatment
Digester
Dewatering system
Sludge

Water scarcity — Water recovery as a need not a wish

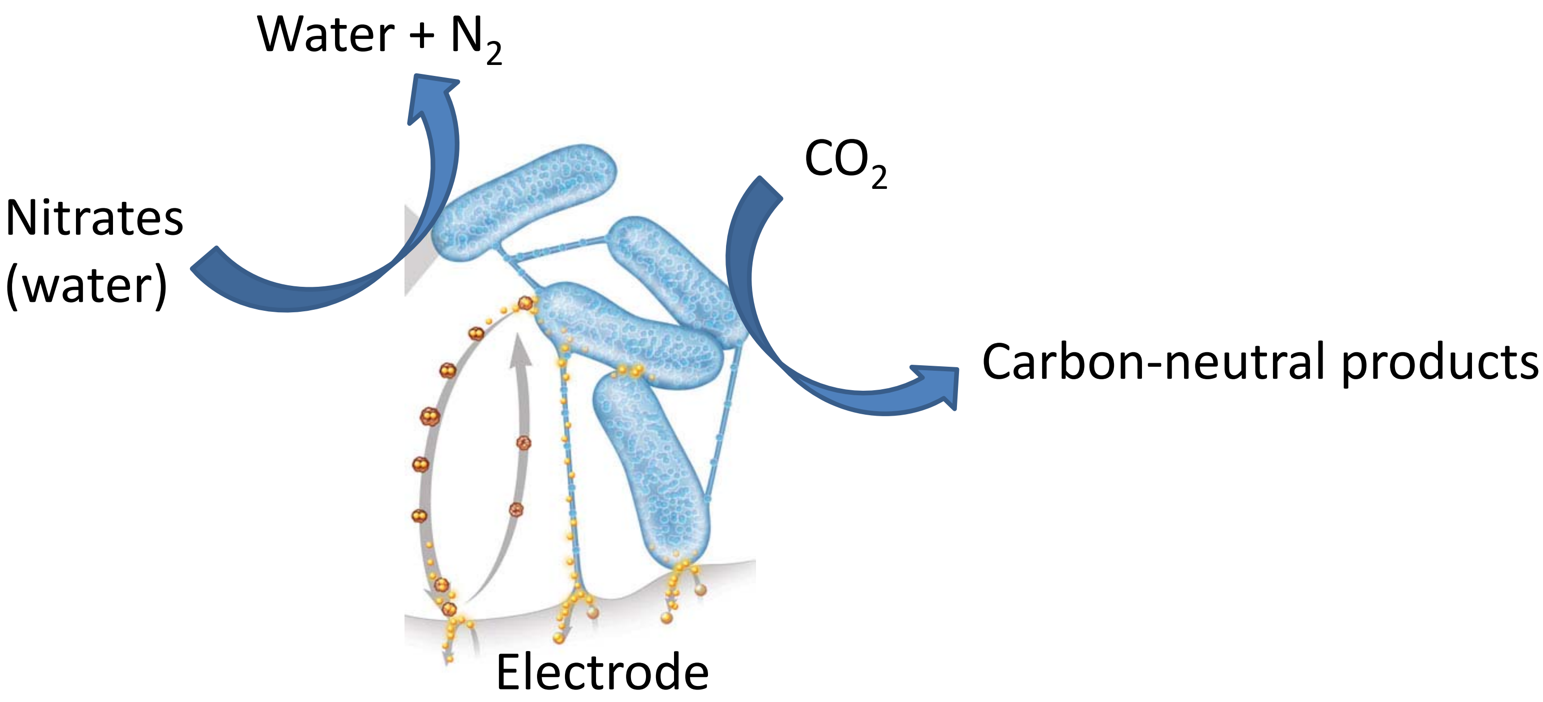


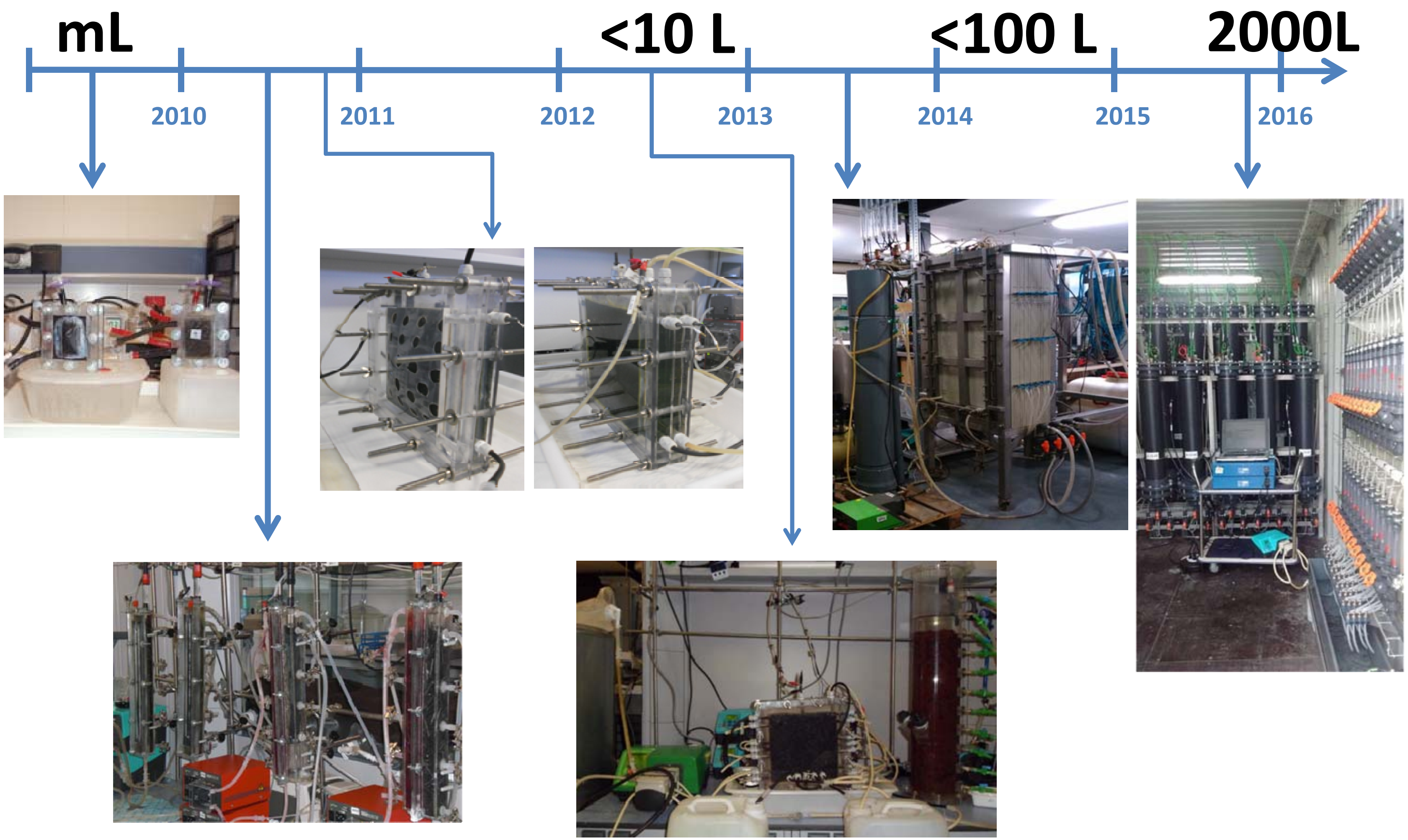
Bioelectroremediation

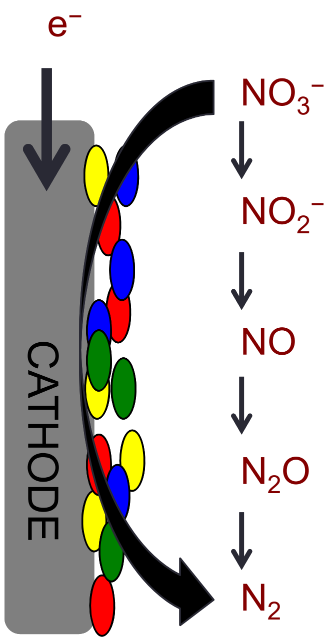
Carbon capture — Carbon transformation

BioelectroCarbon recycling

An **electrotroph** is a microorganism which can receive electrons necessary for its growth from an electrode (power supply) terminal.




mL
<10 L
<100 L
2000L
2010
2011
2012
2013
2014
2015
2016



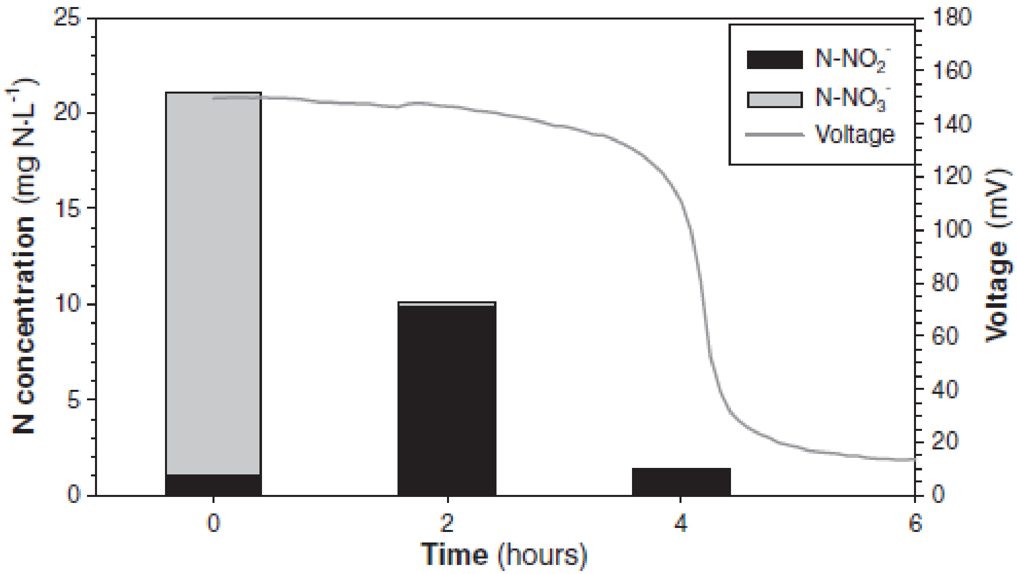
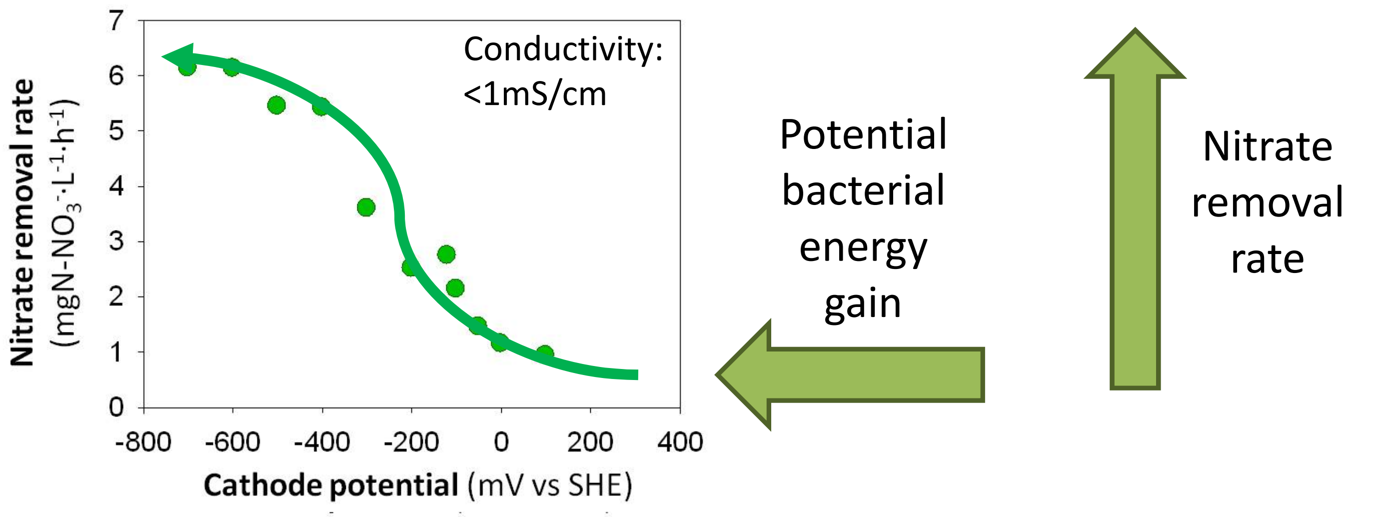


Fig. 2. Relationship between nitrogen compound dynamics and voltage in the denitrifying cathode MFC.

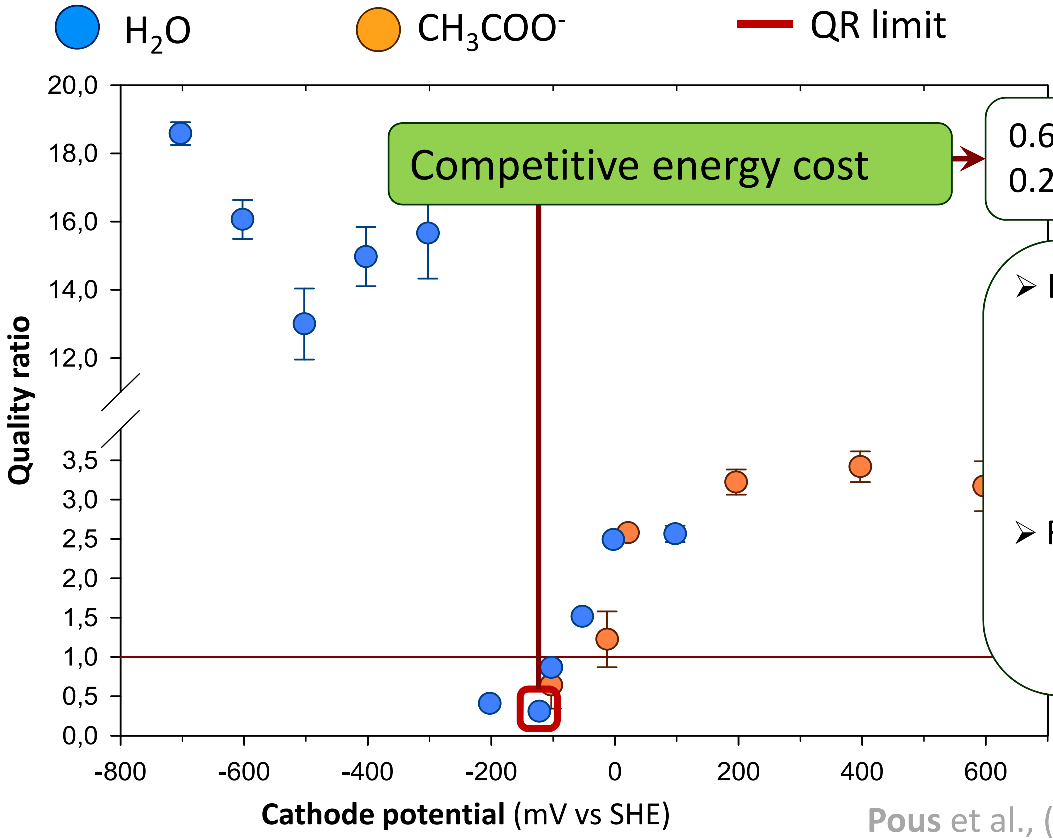
Clauwaert et al. 2007, *Env. Sci. &Technol*
Puig et al. 2012, *Env. Sci. &Technol*. 46 (4), 2309.



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

World Health Organization

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



$0.68 – 1.27·10^{-2}$ kWh·gN-$NO_3^-{}_{rem}{}^{-1}$
$0.20 – 0.38$ kWh·$m^{-3}{}_{treated}$

- Reverse electrodialysis

  $0.40 – 4.95·10^{-2}$ 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)

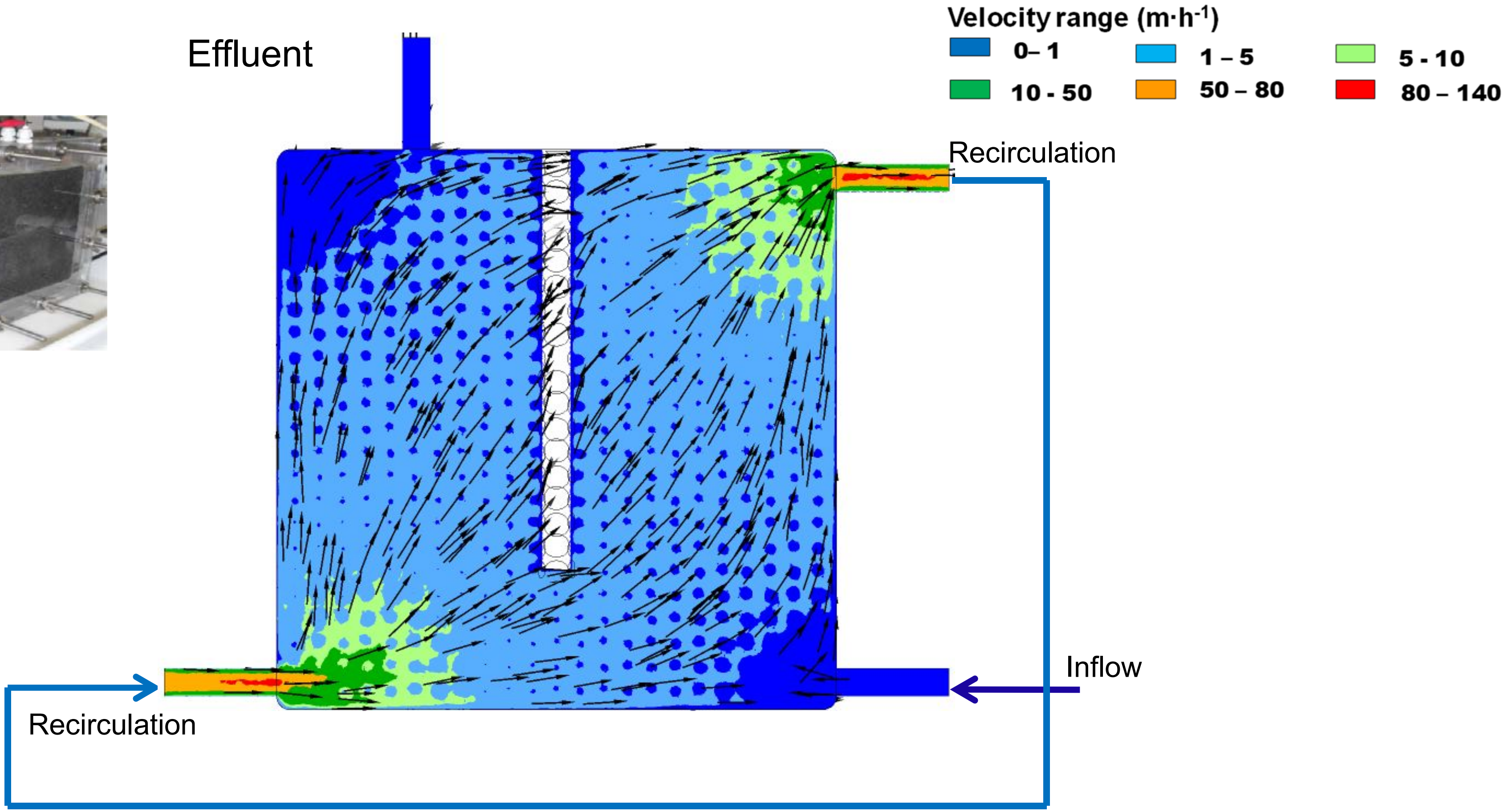
- Reverse osmosis

  $1.03 – 2.09$ kWh·$m^{-3}{}_{treated}$

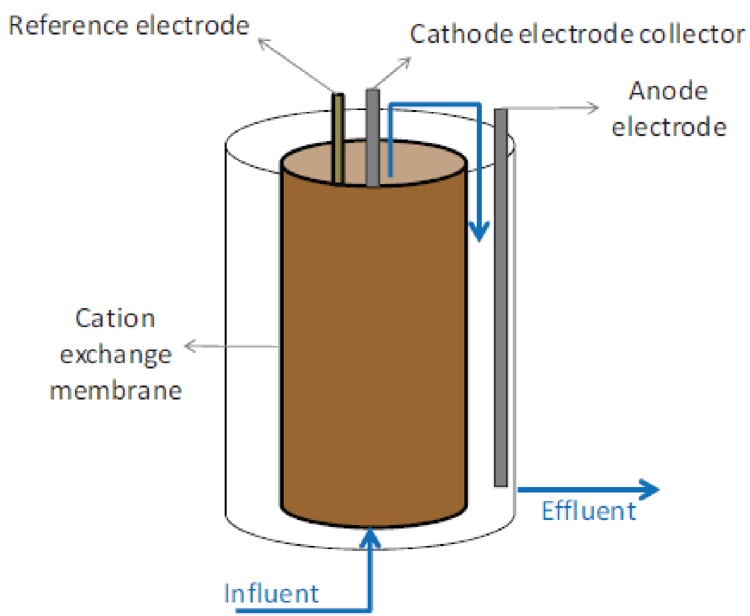
  (Twomey et al., 2010)

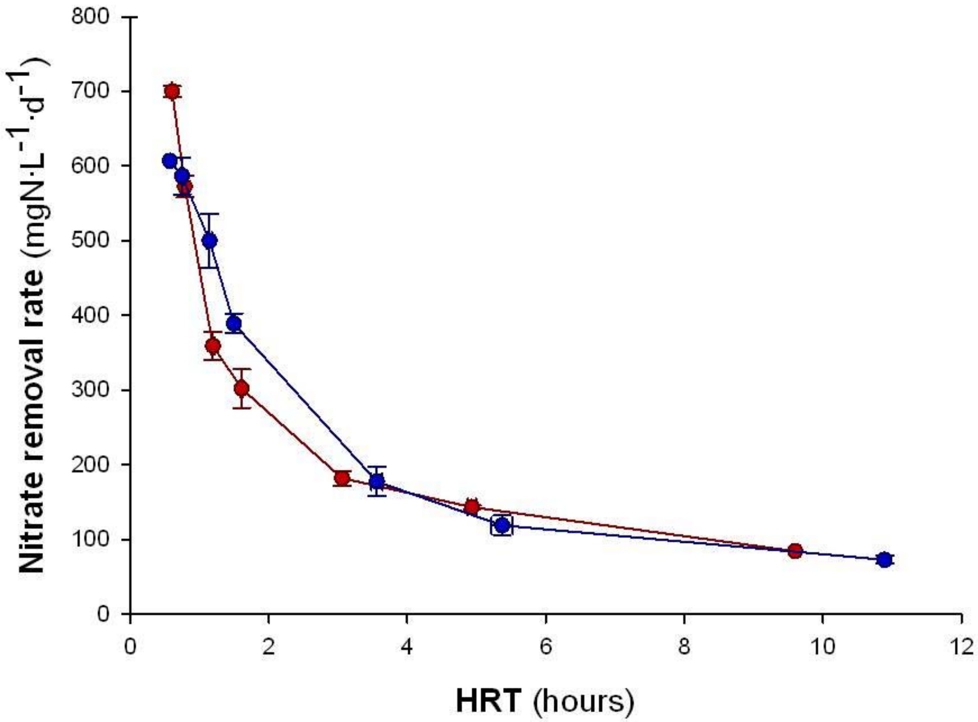
Pous et al., (2015), *Chem. Eng. J. 263, 151-159*

Mass transfer-Hydrodynamics



Vilà-Rovira et al., (2015), *RSC Advances,5 78994–79000*

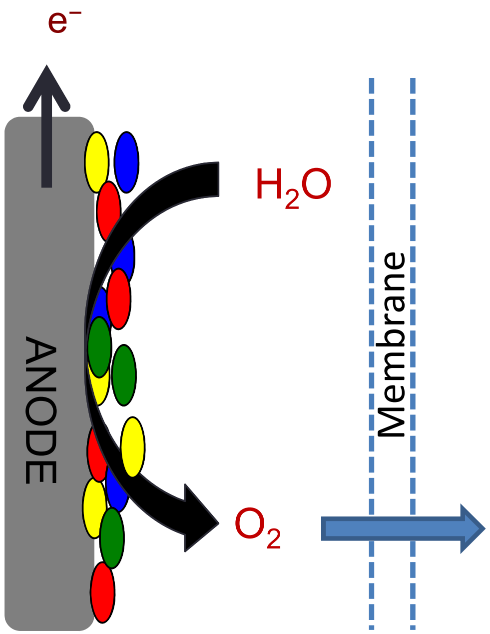

Reference electrode
Cathode electrode collector
Anode electrode
Cation exchange membrane
Effluent
Influent



European Patent
WO 2014082989 A1

Pous et al. Environmental Science: Water Research & Technology 3, 922-929. 2017.

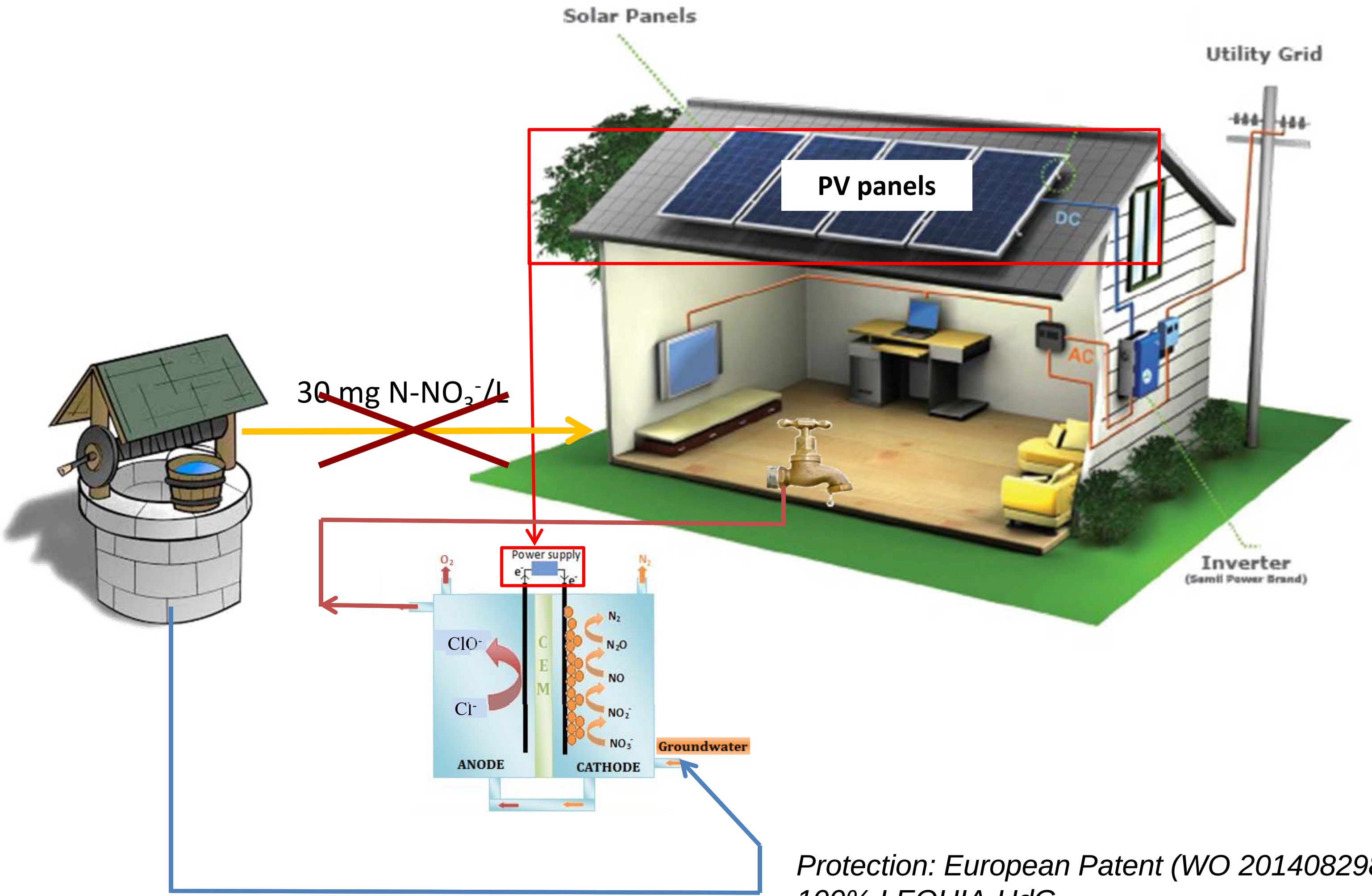
Counter electrode... Side reactions... Opportunities



Anode potential: > + 800 mV vs SHE

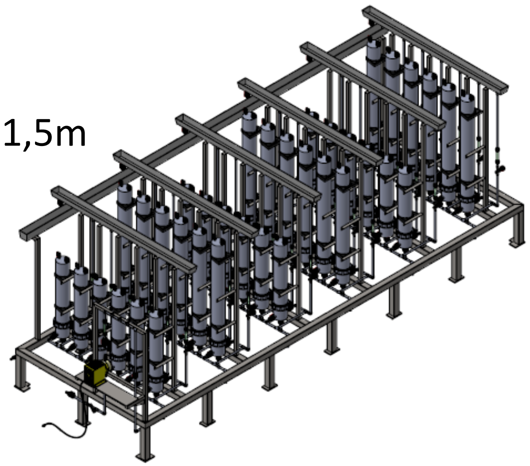
Electron donor	Oxidation reaction (redox potential at pH 7)	Electrode material	Catalysis
Acetate	E0’ = -290 mV vs SHE	Graphite	Biotic
Water	E0’ = +840 mV vs SHE	Graphite	Abiotic
		Stainless steel	Abiotic
Chloride	E0’ = +890 mV vs SHE	Ti-MMO	Abiotic

Contaminant treatment and desinfection using the same tech!



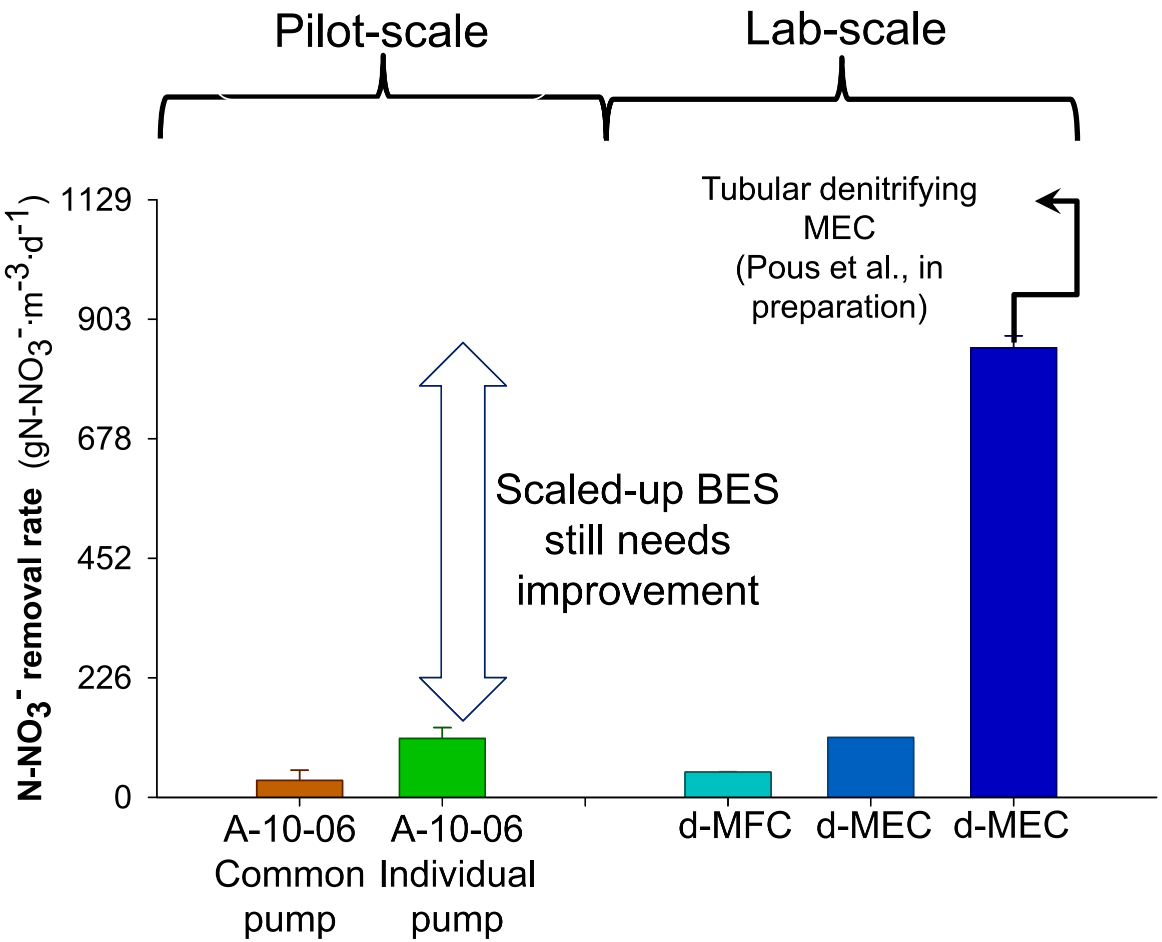
Protection: European Patent (WO 2014082989 A1), 100% LEQUIA-UdG

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



AQUALOGY
Where Water Lives

*TRL-6. Licence contract and demonstration project, **Aqualogy***

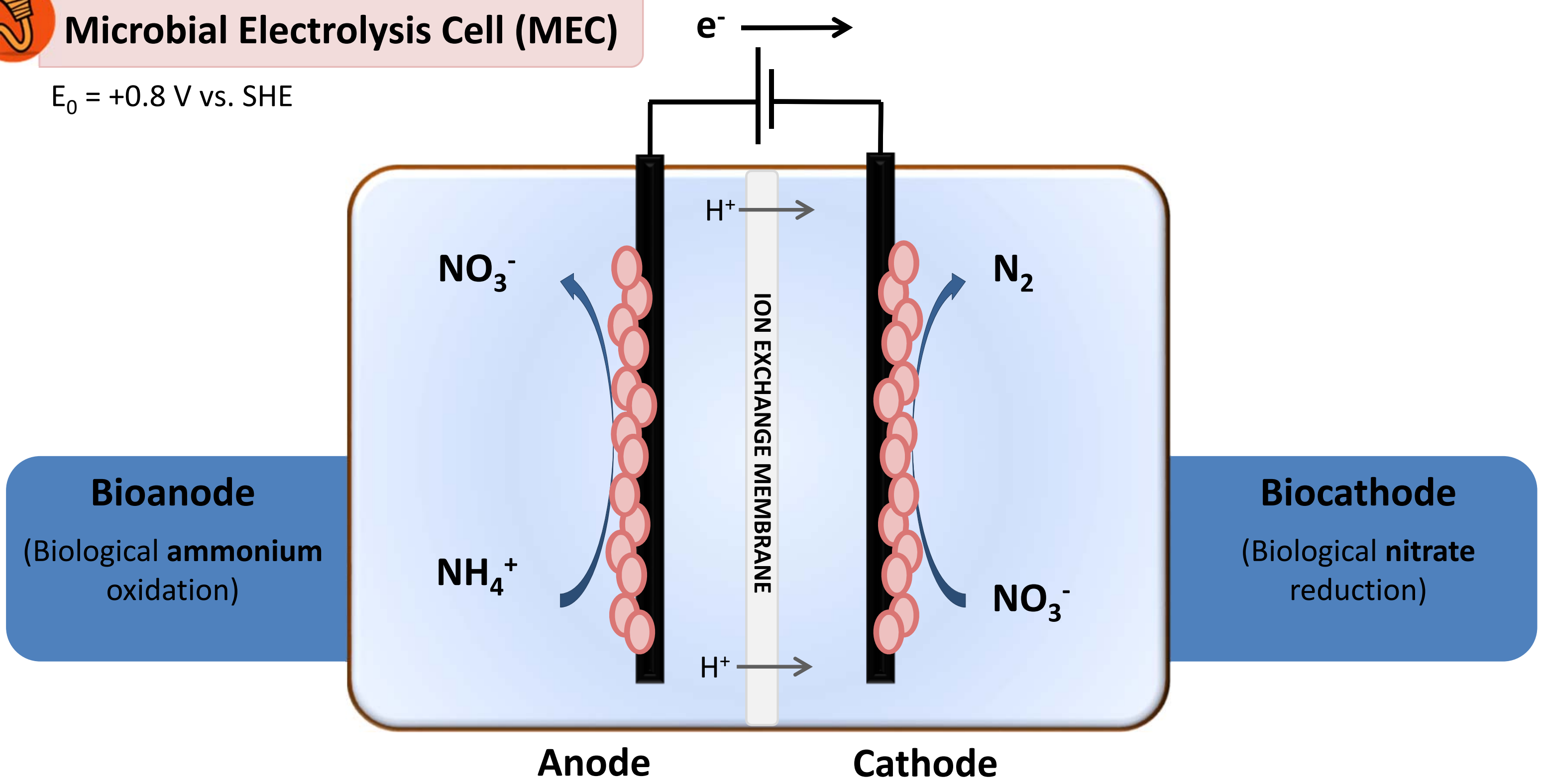


Pilot-scale
Lab-scale
N-NO3- removal rate (gN-NO3-·m-3·d-1)
1129
903
678
452
226
0
Tubular denitrifying MEC (Pous et al., in preparation)
Scaled-up BES still needs improvement
A-10-06 Common pump
A-10-06 Individual pump
d-MFC
d-MEC
d-MEC

Proof-of-concept

Microbial Electrolysis Cell (MEC)

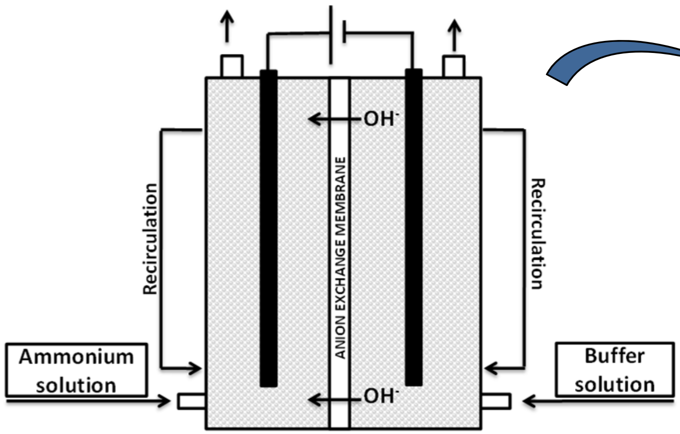
E_0 = +0.8 V vs. SHE

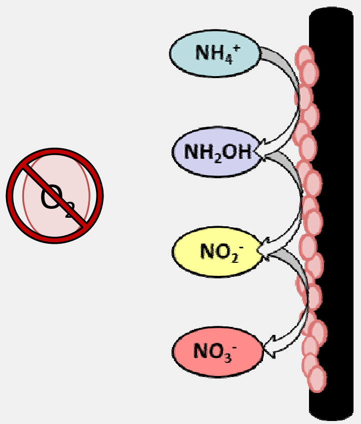


Vilajeliu-Pons et al. Water Research, 2018.

Reactor set-up

Rectangular BES





To demonstrate anoxic ammonium oxidation

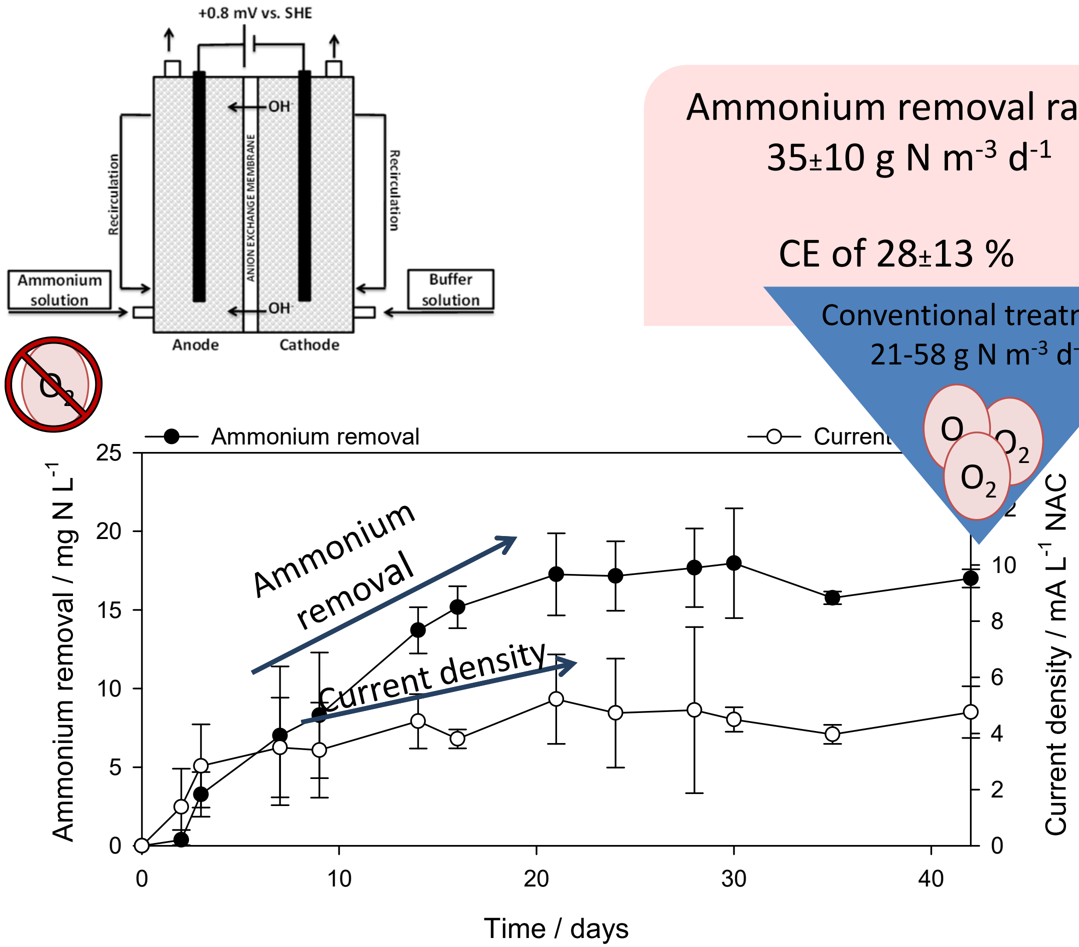
20 x 20 x 2.2 cm
each chamber

460 mL

Graphite electrode

Anion exchange membrane

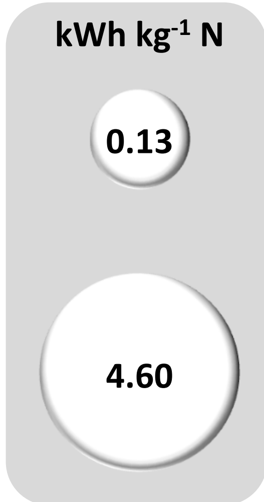
Vilajeliu-Pons et al. Water Research, 2018.



Ammonium removal rate
35±10 g N m^{-3} d^{-1}

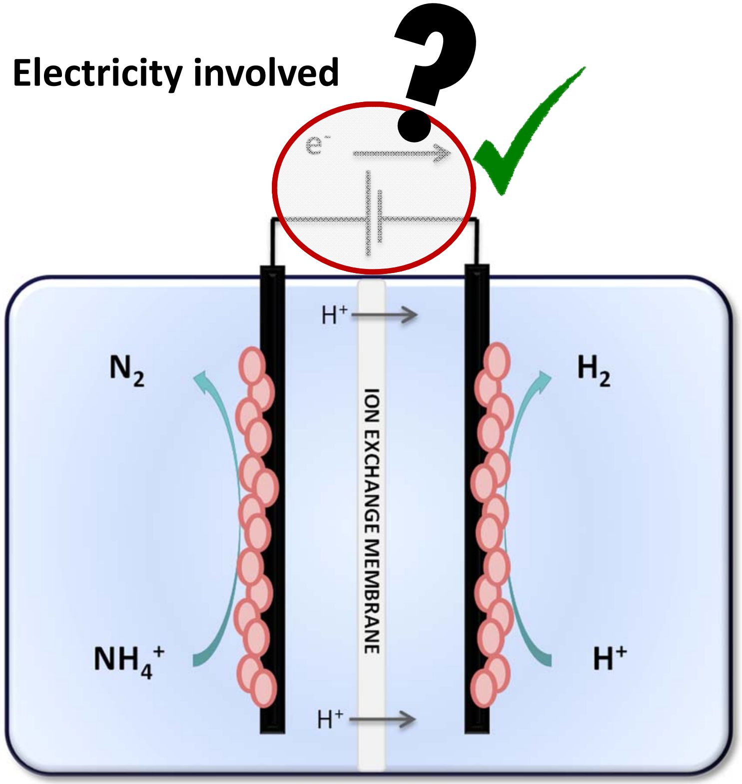
CE of 28±13 %

Conventional treatment
21-58 g N m^{-3} d^{-1}



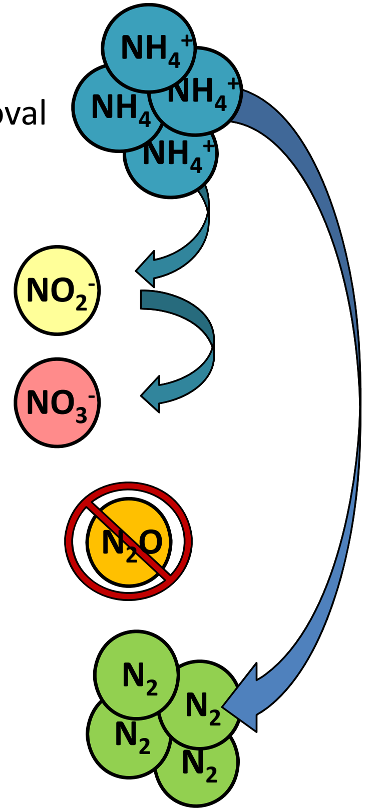
Vilajeliu-Pons et al. Water Research, 2018.

Electricity involved



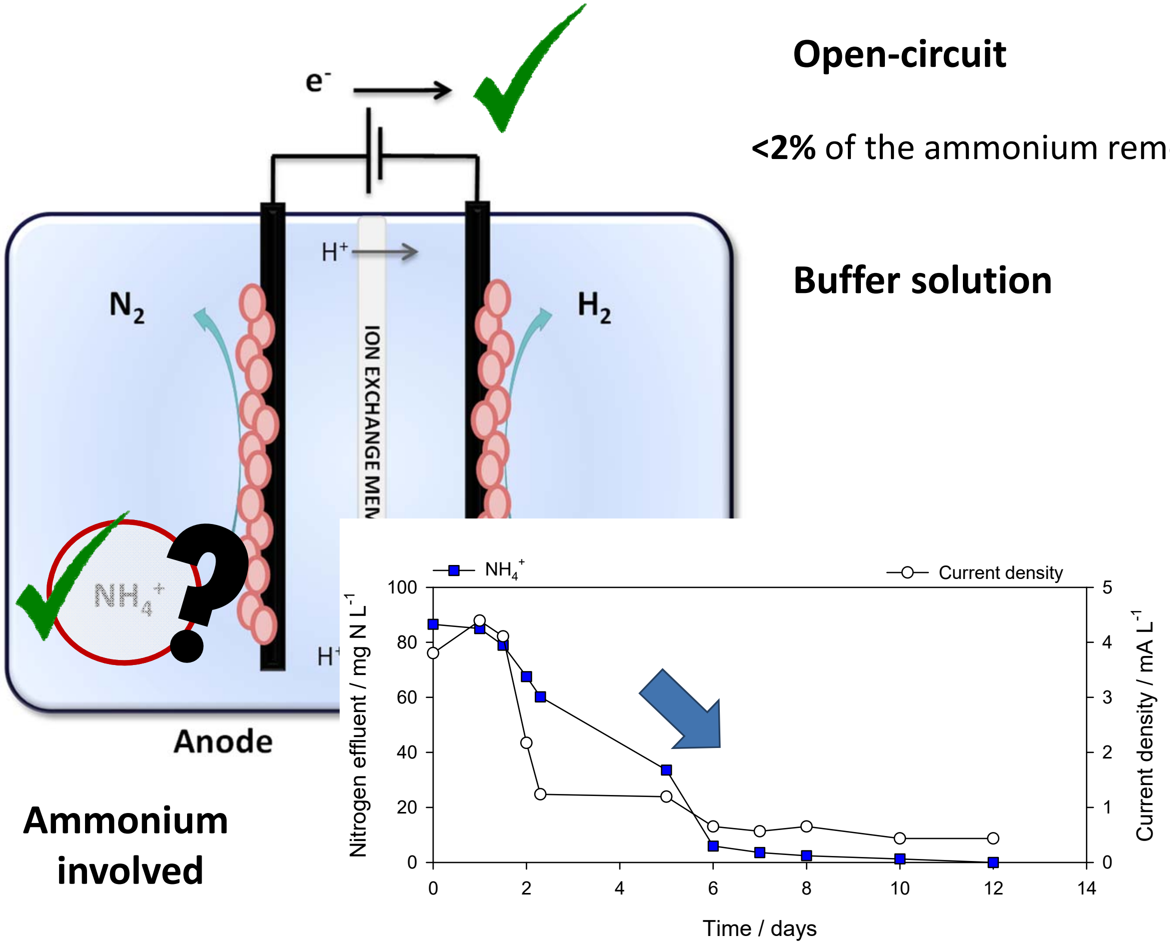
Open-circuit

<2% of the ammonium removal



97% production

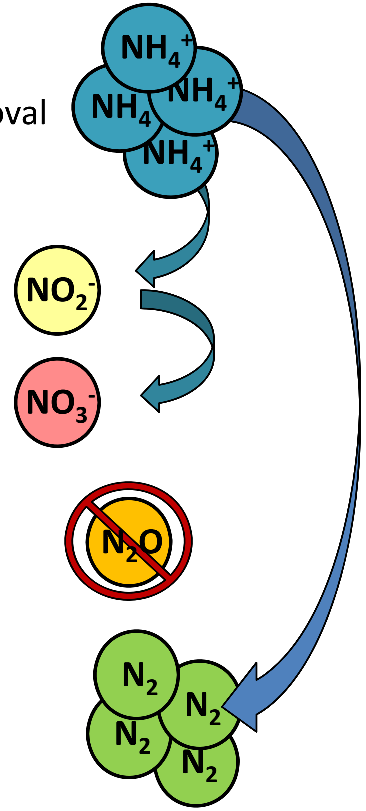
Vilajeliu-Pons et al. Water Research, 2018.



Open-circuit

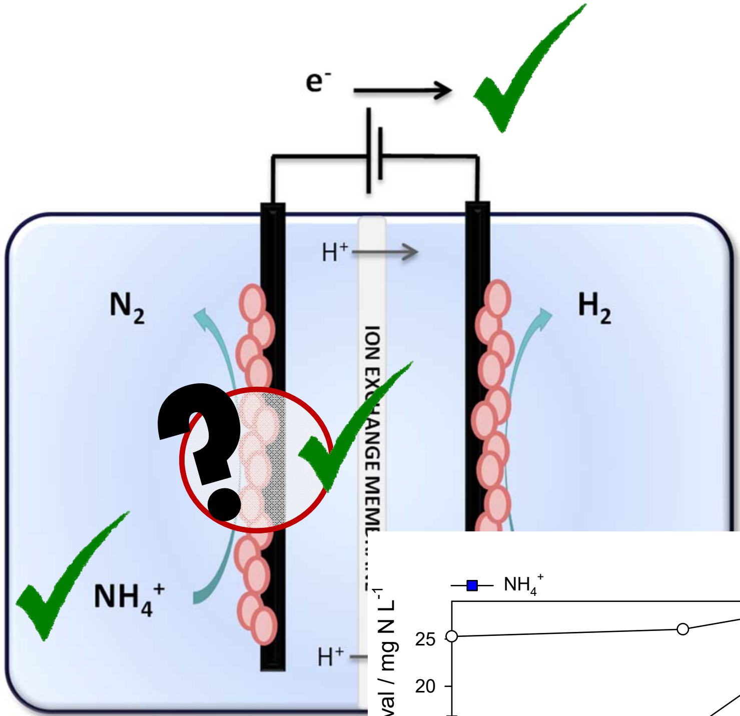
<2% of the ammonium removal

Buffer solution



97% production

Ammonium involved

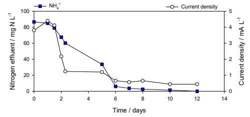


Anode

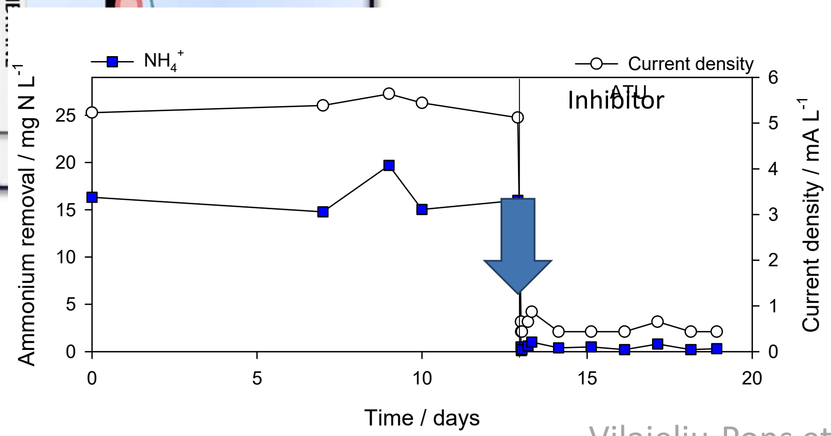
Nitrifying biomass involved

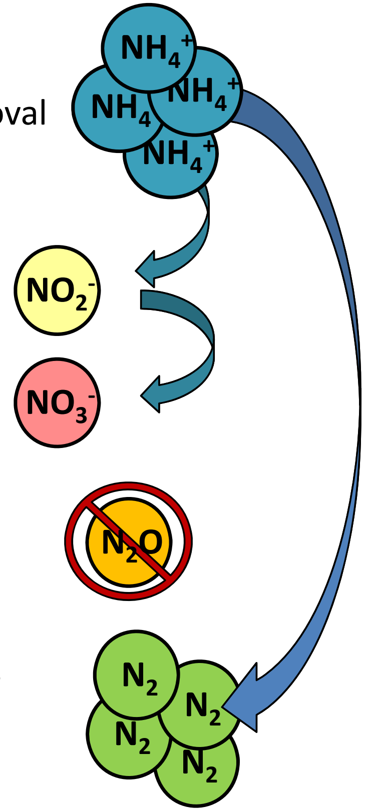
<2% of the ammonium removal

Buffer solution



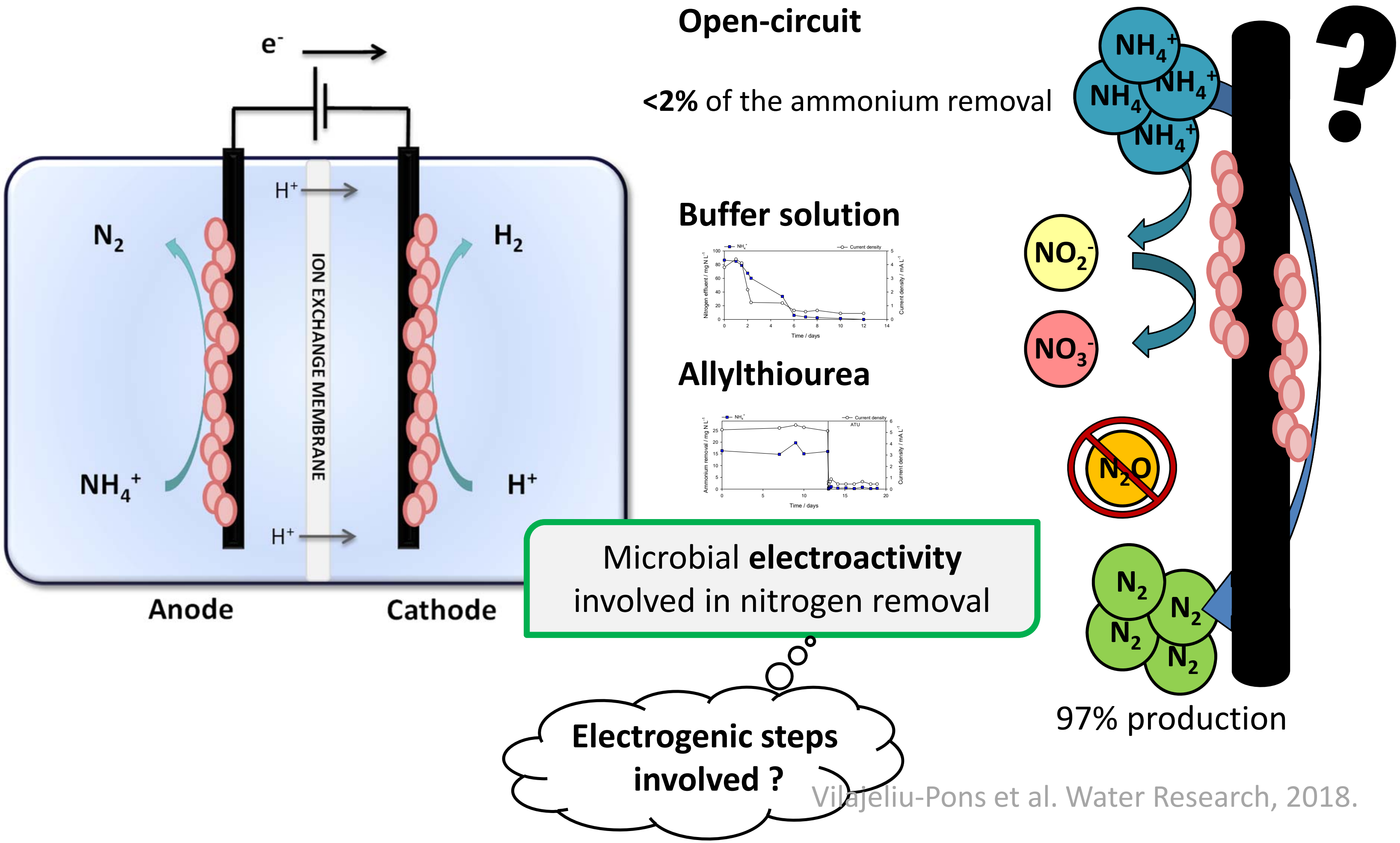
Allylthiourea (ATU)





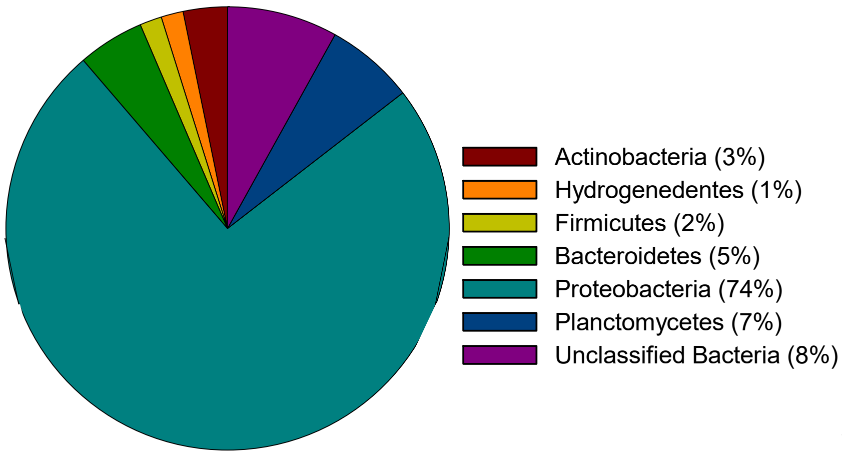
97% production

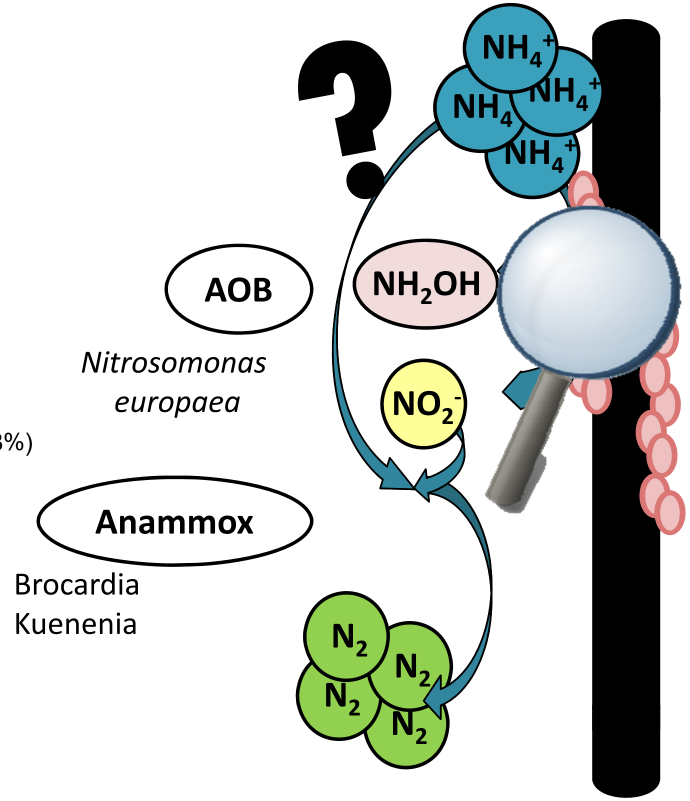
Vilajeliu-Pons et al. Water Research, 2018.



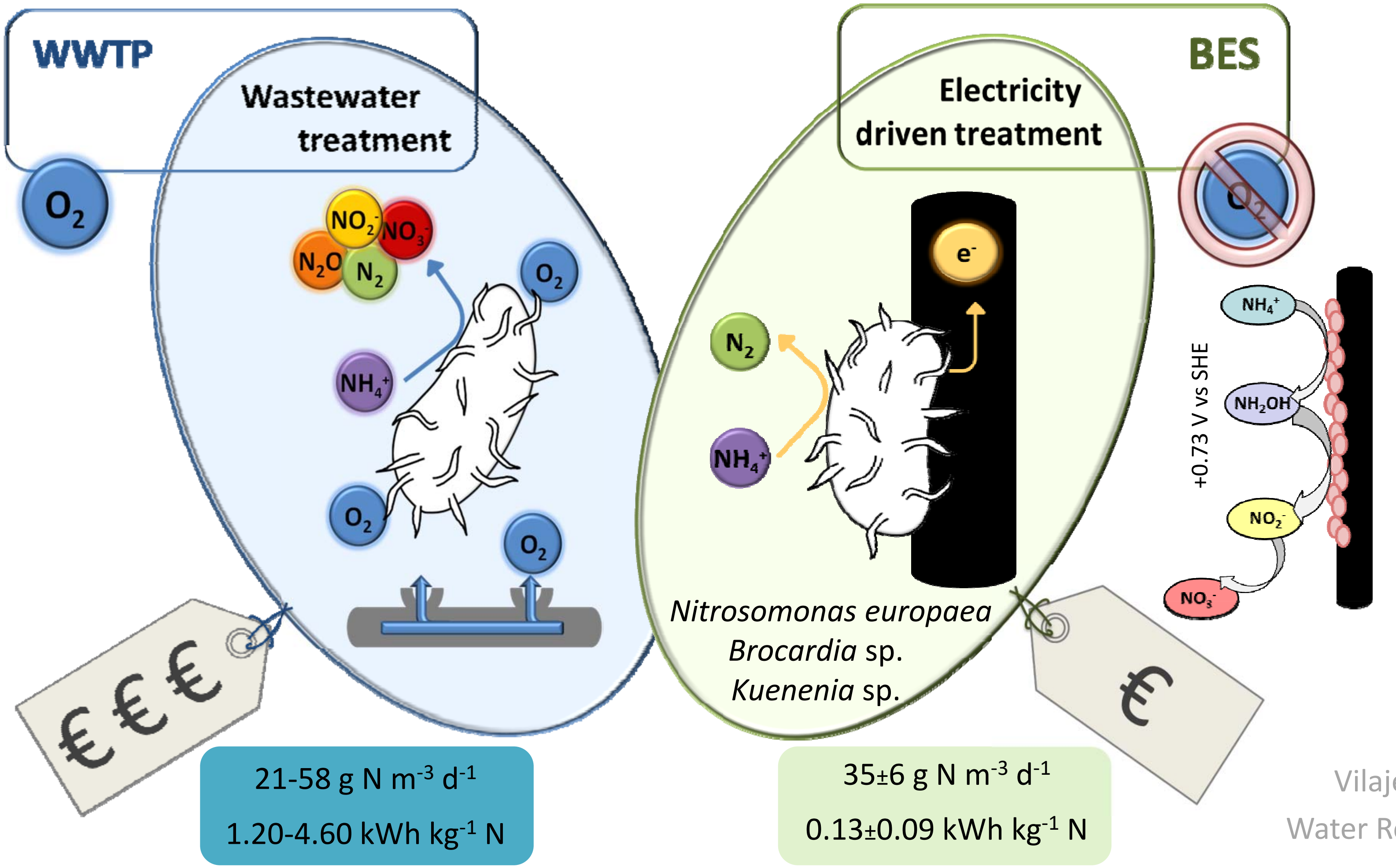
Vilajeliu-Pons et al. Water Research, 2018.

Complex microbial community identified





Vilajeliu-Pons et al. Water Research, 2018.



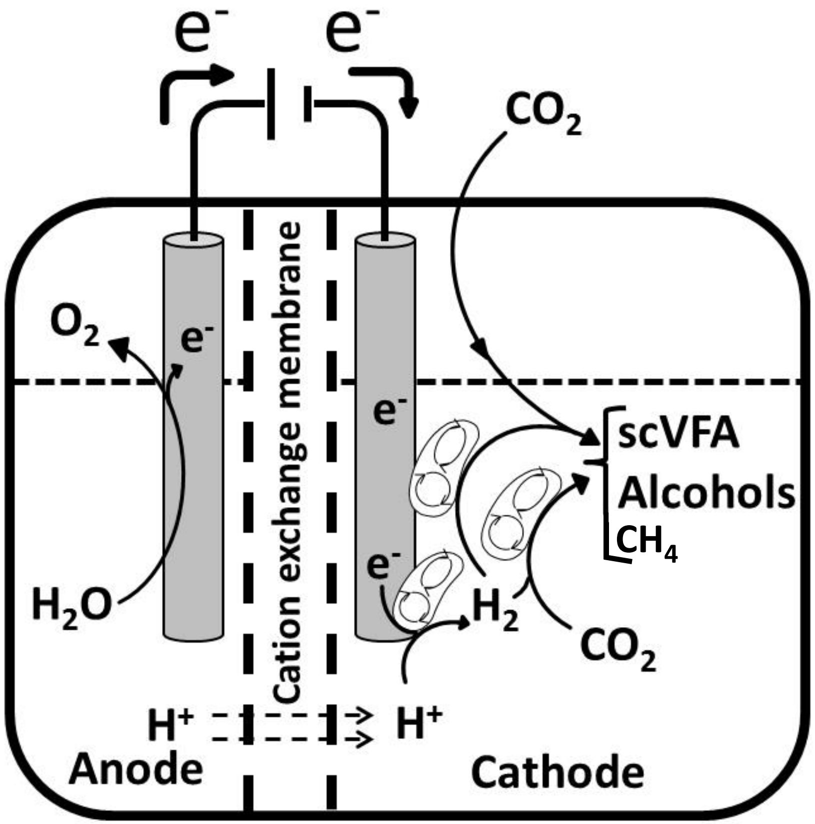
Vilajeliu-Pons et al.
Water Research, 2018.

Carbon capture

Carbon transformation

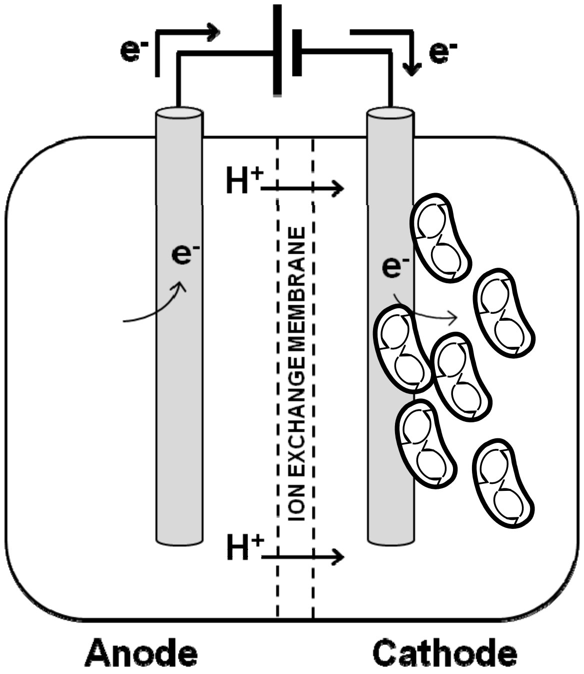
BioelectroCarbon recycling

Electricity-driven reduction of CO_2 using microorganisms as electrocatalyst



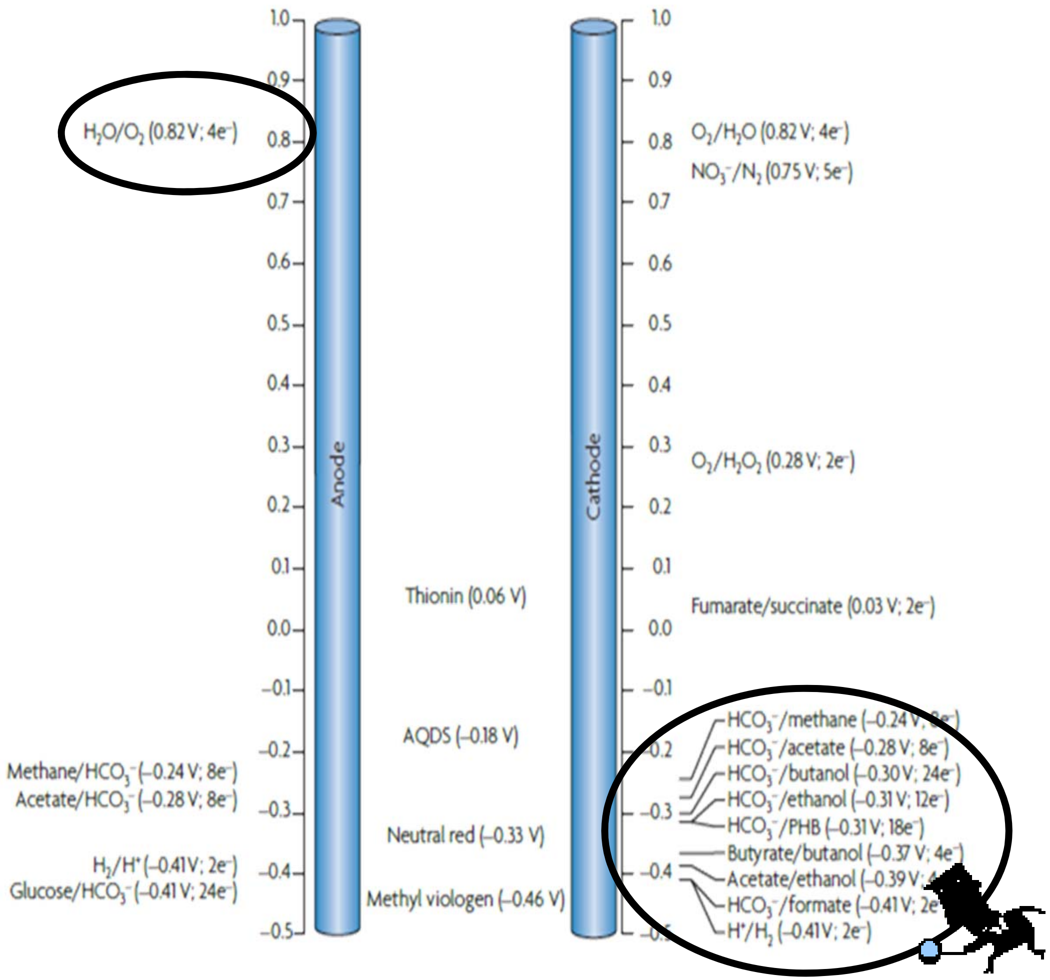
Strengths

- Unlimited **reducing power**
- **Mitigation** and **valorisation of CO_2**
- Low **land usage**
- Renewable **electricity storage**

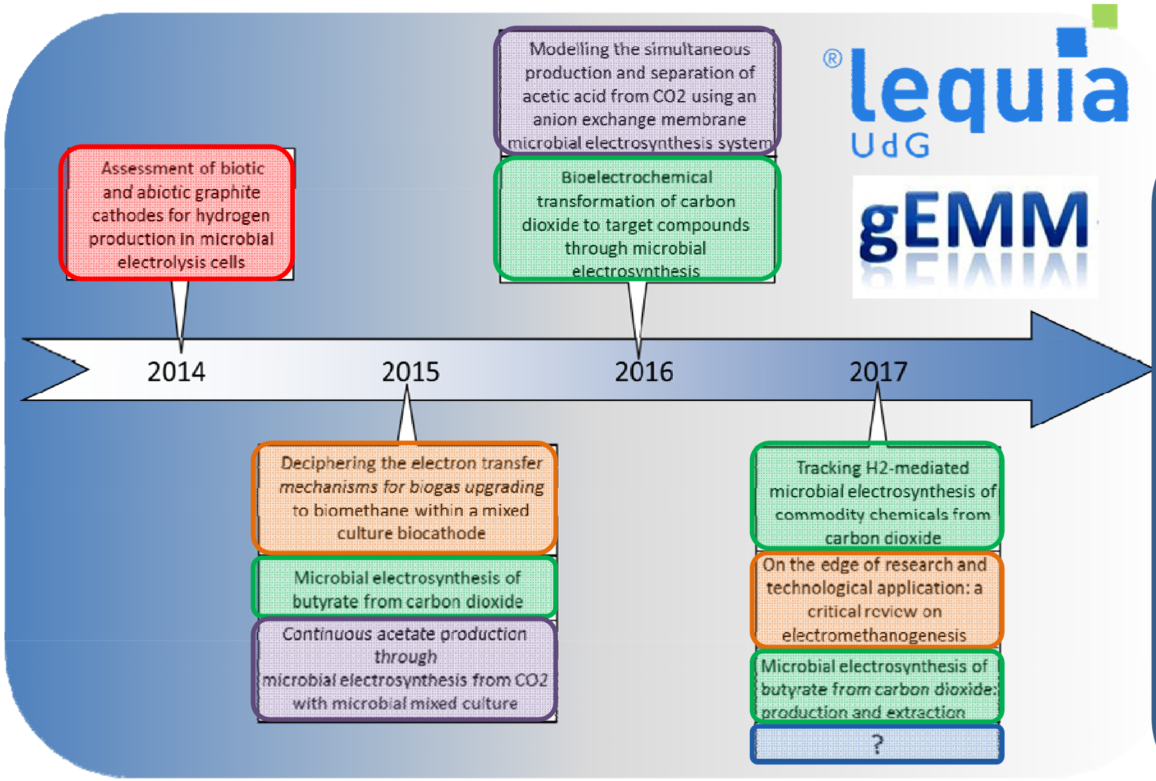


Ecell < 0
ΔG > 0
Non spontaneous

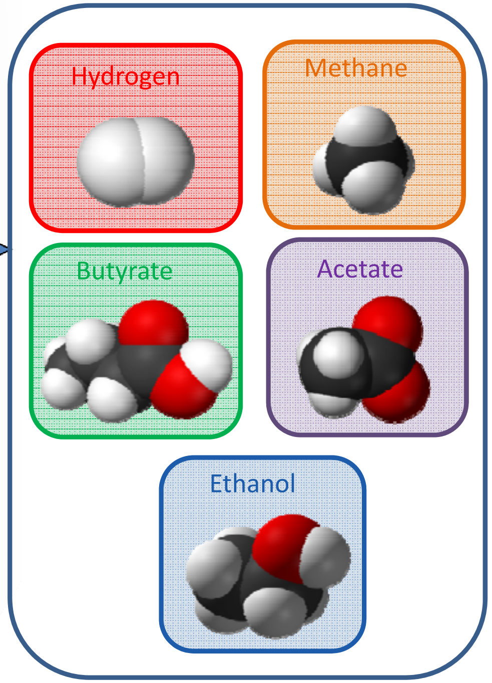
Energy required



Rabaey and Rozendal, 2010. *Nature Rev Microbiol*



Current portfolio

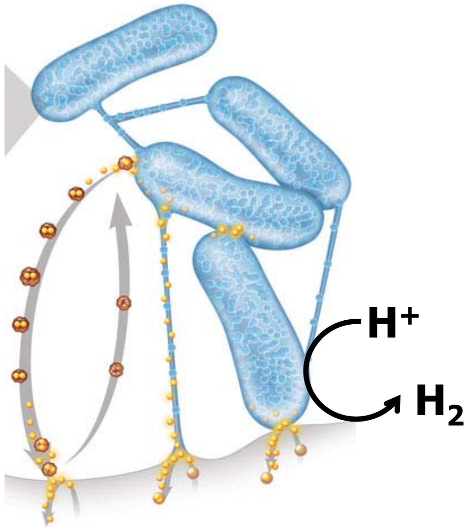


- *Batlle-Vilanova et al. Int. J. Hydrogen Energy. 39 (2014) 1297–1305*
- *Batlle-Vilanova et al. RSC Adv. 5 (2015) 52243– 52251*
- *Ganigué et al. Chem. Commun. 51 (2015) 3235–3238*
- *Batlle-Vilanova et al.. J Chem Technol Biotechnol 91 (2015) 921–927*
- *Matemadombo et al. J Chem Technol Biotechnol (2016)*
- *Puig et al. Bioresour. Technol. 228 (2017) 201-209*
- *Blasco-Gomez et al. Int. J. Mol. Sci. (2017), 18(4), 874*
- *Batlle-Vilanova et al. Bioelectrochemistry. (2017).*

La Plataforma Tecnológica Española del CO2 premia una tesis doctoral del LEQUIA

La investigación de Pau Batlle ha sido reconocida con el premio a la mejor tesis doctoral en tecnologías de captura, almacenamiento y usos del dióxido de carbono

Abiotic vs. **Biotic** mediated H_2 production



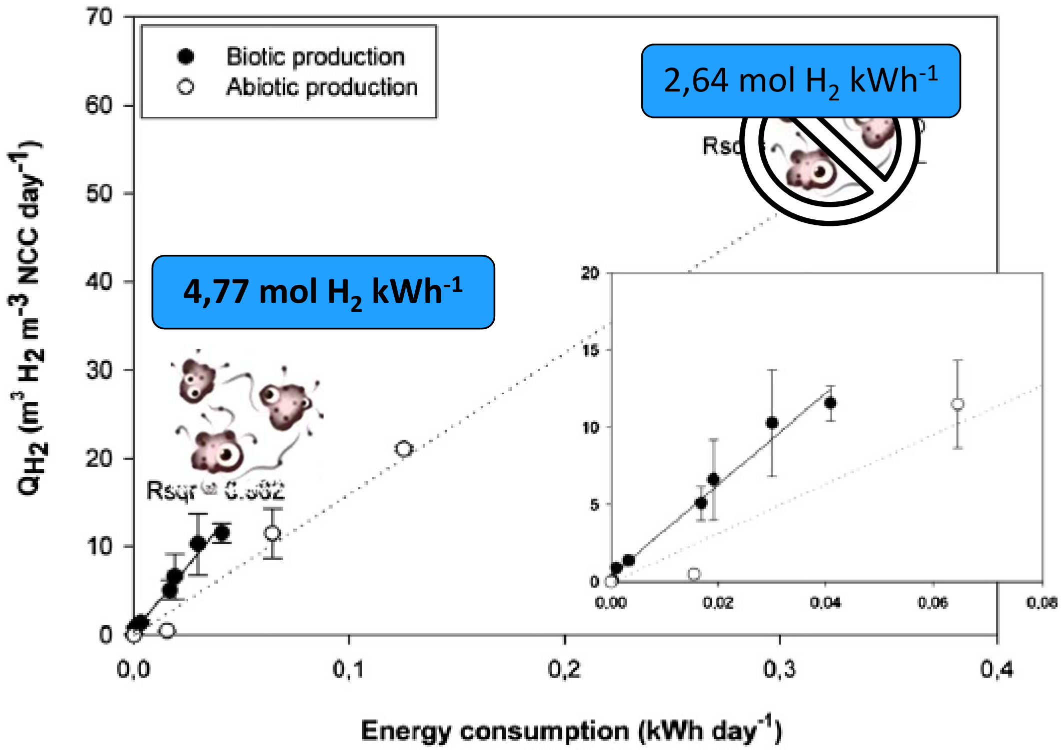
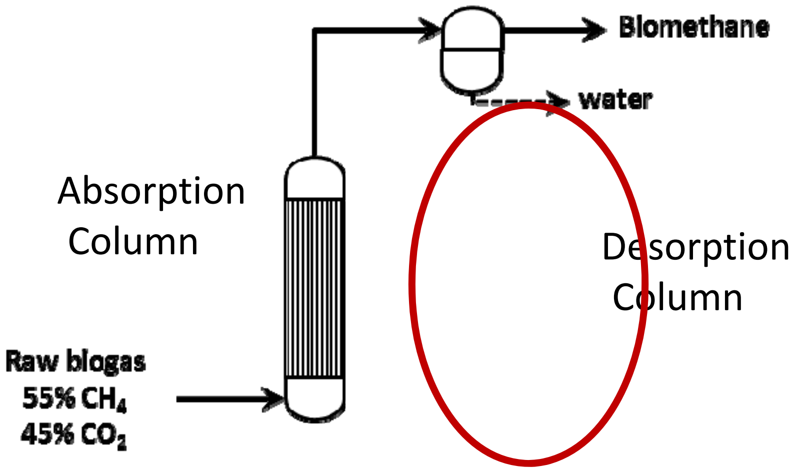
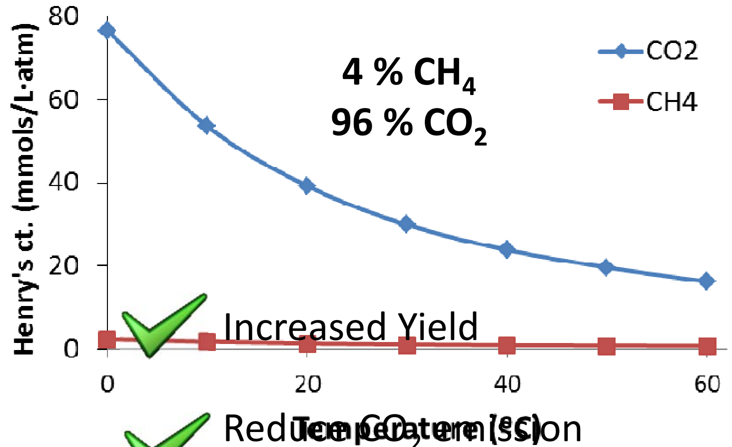


Fig. 2 – Hydrogen production rate versus energy consumed (linear regression fitted) in the biotic and abiotic MEC.

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



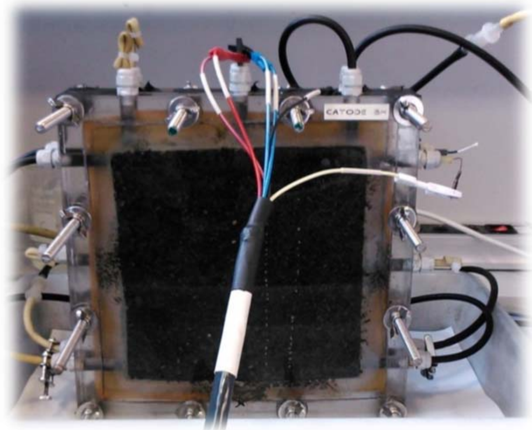


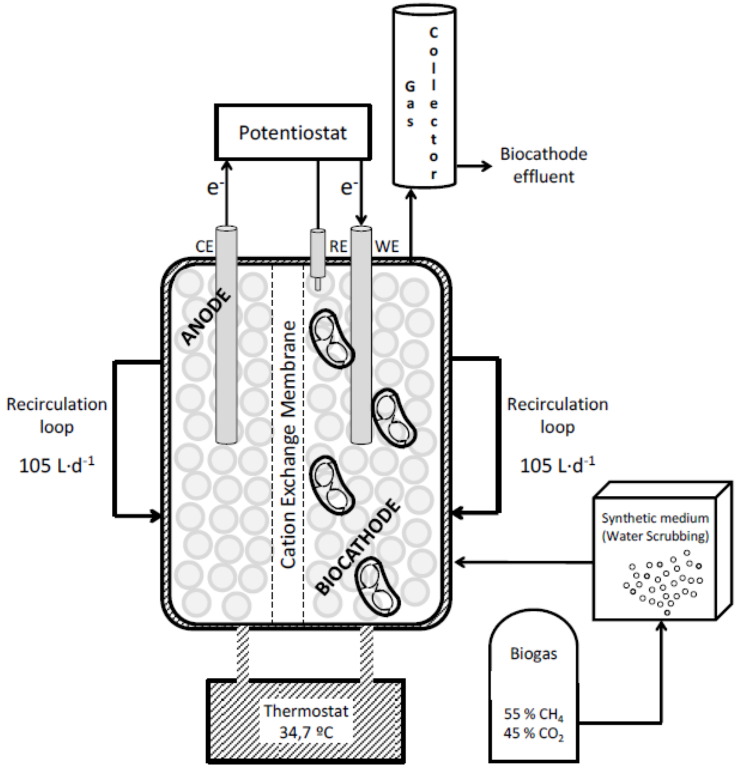
- Increased Yield
- Reduced CO_2 emission

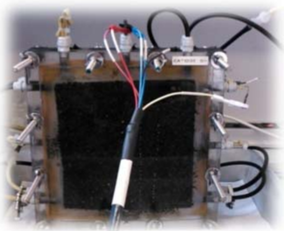
- Energy consumption
- CO_2 emission

Bioelectrochemical

CO_2 transformation







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

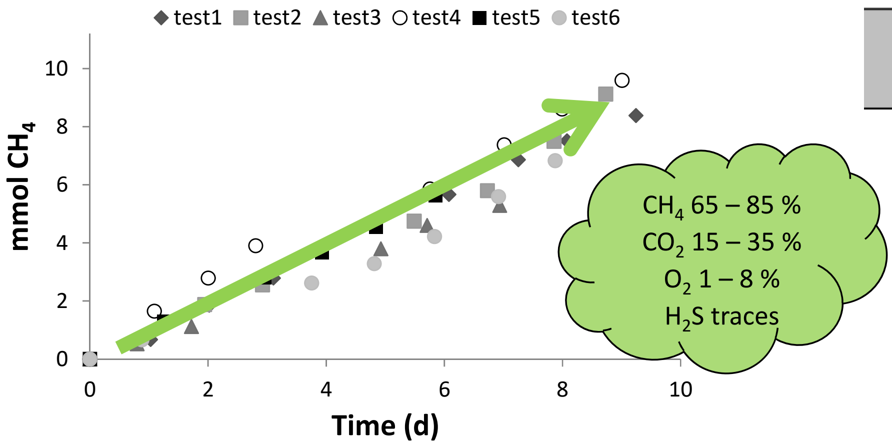
Thermodynamics

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

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

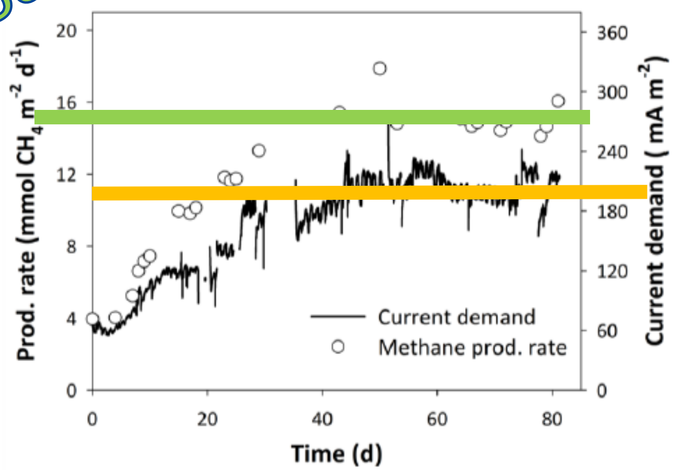
ΔG > 0
Energy required

BATCH



Test	Current demand (mA m^{-2})	pH	Prod rate (mM C d^{-1})	CE (%)
1	32,0	6,1	1,6	45,3
2	40,8	5,9	1,7	39,0
3	31,1	6,3	1,4	47,9
4	32,8	6,1	1,9	45,9
5	27,3	6,0	1,7	51,7
6	31,2	6,8	1,4	54,2
Mean	32,5	6,2	1,6	47,3
St Err	1,8	0,1	0,1	2,2

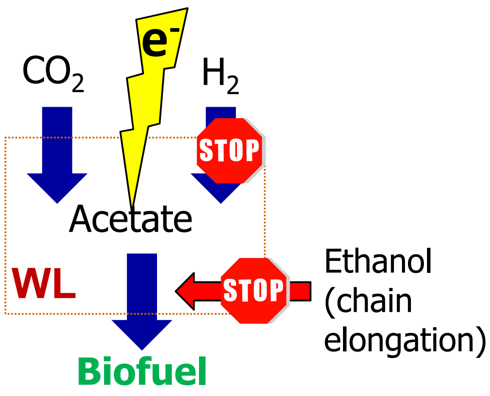
CONTINUOUS



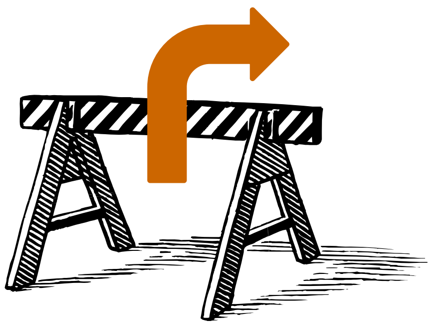
Current demand (A m_{NCC}^{-3})	pH	Prod rate (mM C d^{-1})	CE (%)
201.7 ± 18.1	7.1 ± 0.2	15.4 ± 0.0	68.9 ± 0.8

Challenges to overcome:

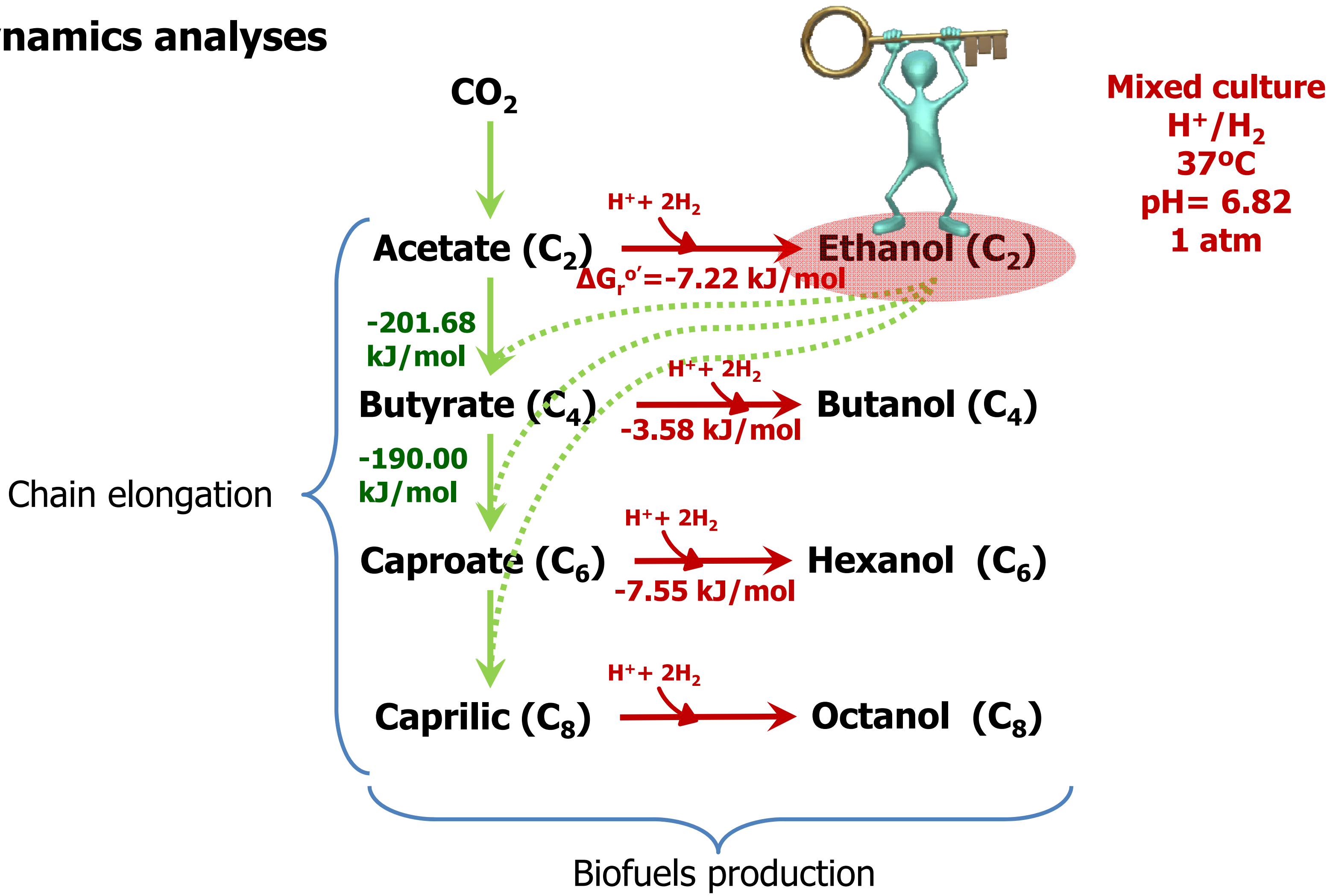
- Limited H_2 availability (reducing power).
- Low solubility of CO_2 and H_2.
- Diverse metabolic routes and products (acids).
- Chemicals needed (ethanol) for carbon chain reactions.



BioElectroCarbon recycling



Thermodynamics analyses



Agler et al. (2011). Trends in Biotechnology

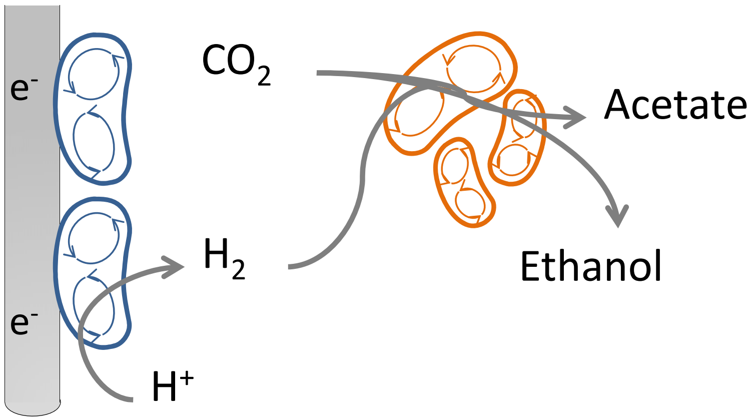
The magic treble

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) *Clostridium scatologenes* K29 (AB610570) *Clostridium drakei* FP (NR_114863.1)	100
2	*Clostridium ljungdahlii* DSM13528 (NR_074161.1) *Clostridium ragsdalei* (DQ020022) *Clostridium autoethanogenum* DSM10061 (CP006763.1)	100
3	Uncultured *Firmicutes* clone (GU559846.1)	94

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



Biofilm ≠ Bulk

Compartmentalization:

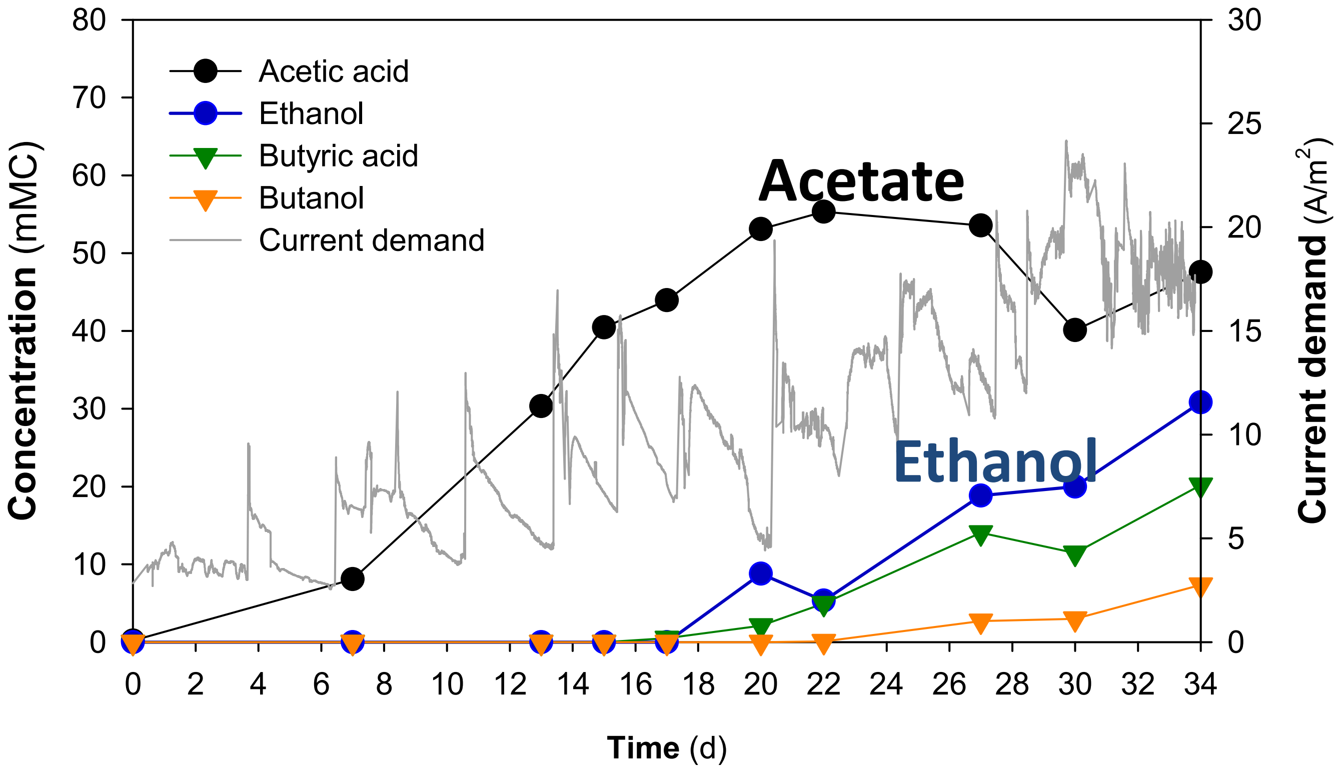
Biofilm community

Bulk community

Puig et al. LEQUIA, 2017. Bioresour. Technol.

BioelectroCarbon recycling

Proof-of-concept



Ganigué et al. 2015. Chem. Comm.

Now… In-line production and extraction

Broth: 87.5 mMC of butyrate and 34.7 mMC of acetate

After extraction:
252.4 mMC of butyrate

Batlle-Vilanova et al. 2017. Bioelectrochemistry

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Moltes gràcies

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