Innovative biological wastewater treatment processes

Anammox process

- Anaerobic ammonia oxidation
- Anaerobic oxidation of ammonia to produce nitrogen gas

$$NH_4^+ + NO_2^- \rightarrow N_2 + H_2O$$

e-donor e-acceptor

- Requires aerobic nitritation of ammonia to NO_2^- for the process to occur (~55% conversion of NH_4 -N to NO_2 -N)
- By autotrophic bacteria
 - → No organic carbon consumption during the process

Anammox process

$$NH_4^+ + NO_2^- \rightarrow N_2 + H_2O$$

- Proposed metabolic model (Van de Graaf et al., 1997)
 - 1) Reduction of nitrite to hydroxylamine (NH₂OH)
 - 2) Condensation of hydroxylamine with ammonium to hydrazine (N_2H_4)
 - 3) Oxidation of hydrazine to nitrogen gas
- Some formation of NO₃-N from NO₂-N
 - To provide the reducing power to fix CO₂

$$CO_2 + 2NO_2^- + H_2O \rightarrow CH_2O + 2NO_3^-$$

Overall reaction (Strous et al., 1999)

$$1.0NH_4^{+} + 1.32NO_2^{-} + 0.066HCO_3^{-} + 0.13H^{+}$$

$$\rightarrow 1.02N_2 + 0.26NO_3^{-} + 0.066CH_2O_{0.5}N_{0.021} + 2.03H_2O_{0.5}N_{0.021} + 0.066CH_2O_{0.5}N_{0.021} + 0$$

Anammox process

Microorganisms for anammox

- Forms dense granular flocs
- Slowly growing (low Y value)
- High bacterial concentration (10¹⁰~10¹¹ cells/mL) should be maintained for good anammox activity

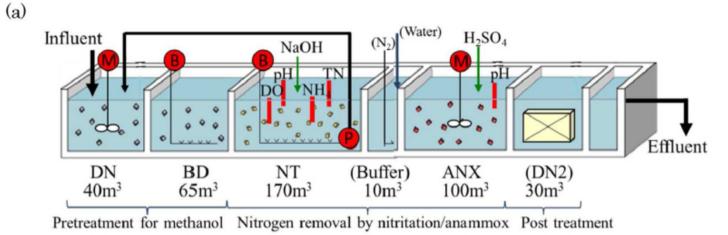
Advantages

- Substantially lower aeration requirement \rightarrow low cost, low carbon footprint
- Low sludge production
- Good sludge settling properties

Limitations/challenges

- Long time required for process setup/recovery after sludge loss
- Optimum pH = $8 \rightarrow$ may need chemical input
- Difficult to achieve partial nitrification (nitritation)





DN: denitrification; BD: BOD oxidation; NT: nitritation; ANX: anammox

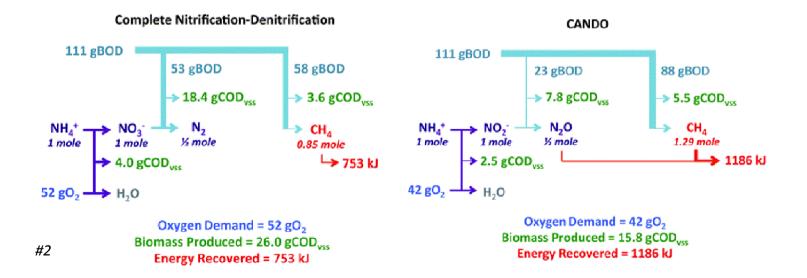
(b) Inside of anammox reactor



Fig. 1. (a) Schematic diagram and (b) photograph of full-scale anammox plant using gel carriers.

CANDO process

- Coupled Aerobic-anoxic Nitrous Decomposition Operation
- A recently proposed process (Scherson et al., Energy Environ. Sci., 2013)
- Three-step process
 - 1) Partial nitrification of NH_4^+ to NO_2^- (same as the prelim. step for anammox)
 - 2) Partial anoxic reduction of NO₂- to N₂O
 - 3) N_2O conversion to N_2 with energy recovery (e.g., use as an oxidant for $CH_4 \rightarrow CO_2$)
- Pilot-scale demonstration underway



6

Aerobic granular sludge

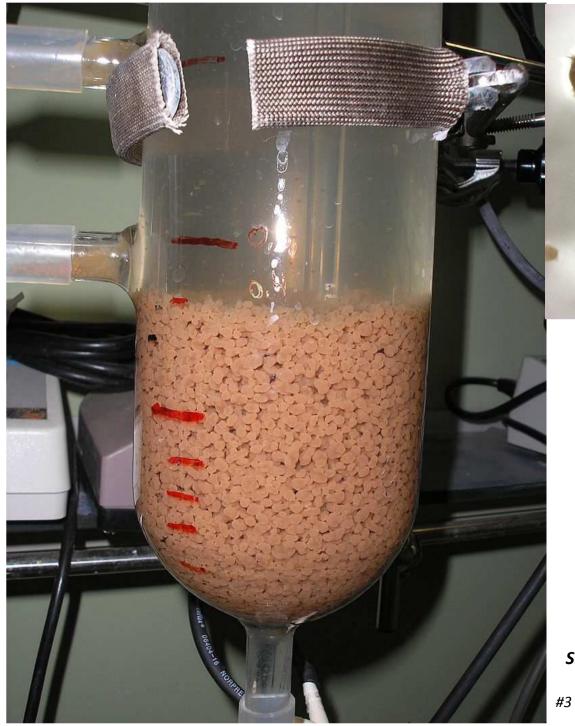
Basic concept

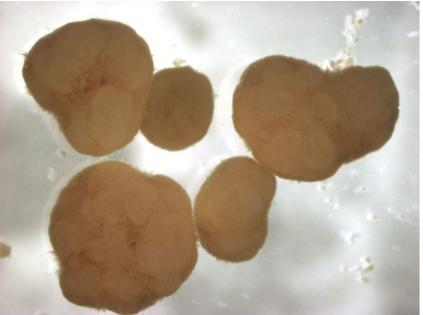
 Grow and utilize microbial "granules", which are compact and dense aggregates, instead of microbial "flocs" used in conventional activated sludge

Parameter	Activated sludge	Aerobic granular sludge
Shape and average size	Irregular; Small, ~<0.2 mm	Large mm-sized distinct particles with well-defined spherical shape; >0.2 mm
Specific gravity	0.997-1.01	1.010-1.017
Settling velocity	Lower settling velocities ~<10 m/h	Higher settling velocities >10 m/h
Microenvironment within the particle	Minimum possibilities for anaerobic zones	Distinct layers or microenvironments i.e., aerobic, anaerobic and anoxic zones

Aerobic granular sludge: Operational scheme

- Usually employed in sequential batch reactor (SBR) settings
- Operation requirements to accomplish granulation
 - Feast-famine feeding regimes: expose microorganisms to alternating condition of presence/absence of organic matter → granule formers are competitive at this condition (can store organic matter in cells during the famine period)
 - Hydrodynamic shear force: high shear forces favor the granule formation and improve the physical granule integrity
 - Short settling time: selectively collect granules while flushing out flocs





Aerobic granules

#3

SBR with aerobic granules

9

Aerobic granular sludge: Advantages

Stability

Good performance with shock and fluctuating organic loading

Low energy requirement

- High aeration efficiency
- Neither sludge return nor nitrate recycle streams required

Low space requirement

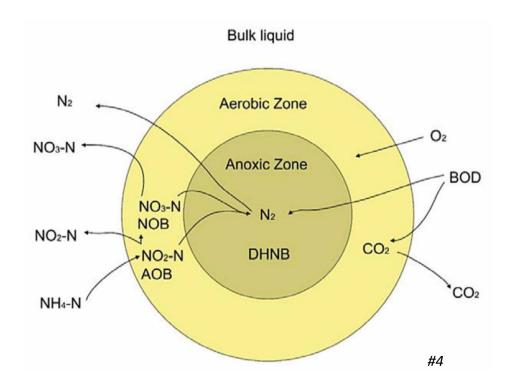
- High organic loading rate (OLR) due to high biomass concentration
- Clarifier not required

Simultaneous removal of BOD & N/P

- Layer of microenvironments formed within the granule
- → simultaneous nitrification-denitrification: aerobic/anoxic
- → enhanced biological phosphorus removal (EBPR): aerobic/anaerobic

Simultaneous nitrification and denitrification

- In microbial flocs, granules, or biofilm
- Local conditions in the floc/granule/biofilm may be different from bulk liquid
 - High DO at the exterior and low DO inside → conditions for nitrification and denitrification may develop
- Can be significant if optimal conditions are developed



Aerobic granular sludge: Current status

- Adapted for industrial applications from mid 2000s
- Full-scale demonstration plants in South Africa and Portugal in late 2000s
- Application for scaled-up domestic sewage treatment plants from 2010



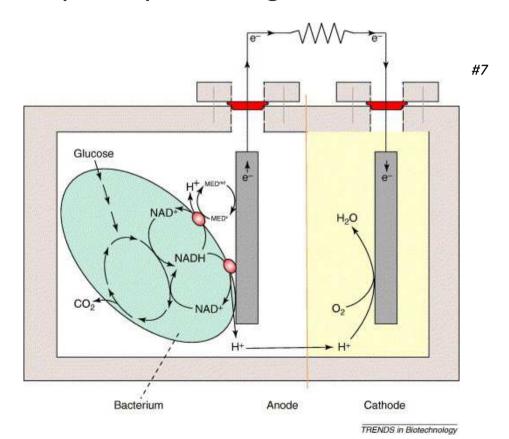
WWTP in Epe, the Netherlands (2010~)



WWTP in Garmerwolde, the Netherlands (2010~)

Microbial Fuel Cell (MFC)

- A device that converts the chemical energy to electrical energy by the action of microorganisms
- The redox reaction is catalyzed by microorganisms



cf) Fuel cell

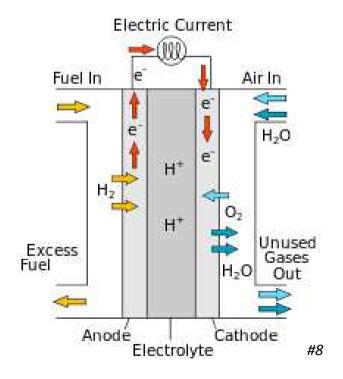
- A device that converts the chemical energy from a fuel into electricity through an electrochemical reaction of hydrogen with oxygen or another oxidizing agent
- Each half reaction of the overall redox reaction occurs separately at each electrode
 - Oxidation half reaction (Anode)

ex)
$$\frac{1}{2}H_2 \rightarrow H^+ + e^-$$

Reduction half reaction (Cathode)

ex)
$$\frac{1}{4}O_2 + H^+ + e^- \rightarrow 2H_2O$$

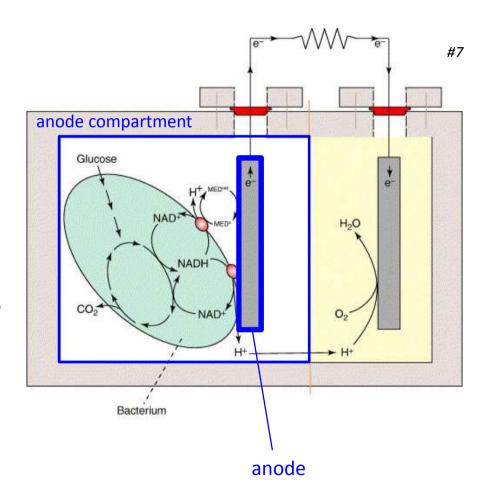
- Electrons move through the electric circuit (electricity generated)
- H⁺ move through the electrolyte



MFC – Anode compartment

Anode

- Should be conductive, biocompatible, chemically stable with substrate
- Stainless steel mesh, graphite plates or rods
- Bacteria live in the anode compartment and oxidize the substrate provided
- Anode compartment should be kept low in DO
- Substrates: usually organics carbohydrates, protein, VFAs, cellulose, and wastewater



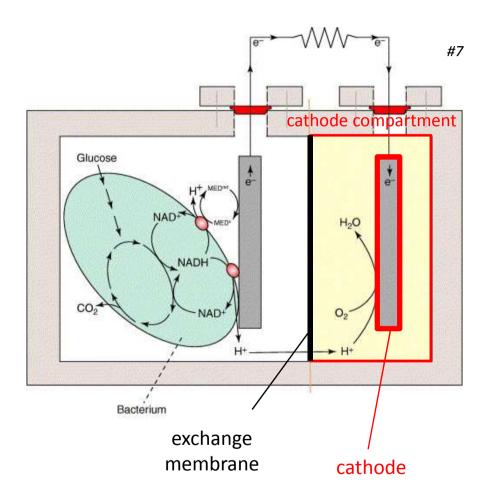
MFC – Cathode compartment / EM

Cathode compartment

- Usually oxygen is used as an oxidizing agent
- Catalysts used for the oxygen reduction reaction: Pt most common

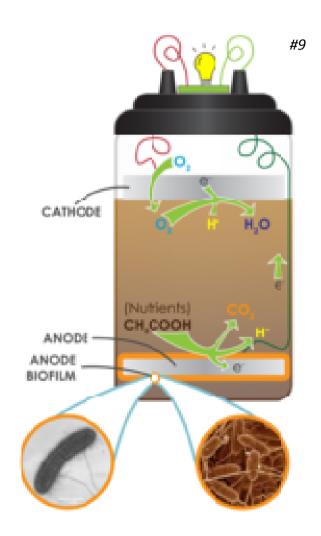
• Exchange membrane

 Allows proton (H⁺) to flow from the anode compartment to cathode compartment



Soil-based MFCs

- Soil serves as
 - Anode compartment
 - Proton exchange membrane
- And soil provides
 - Microorganisms
 - Nutrients



MFC – pros & cons

Advantages

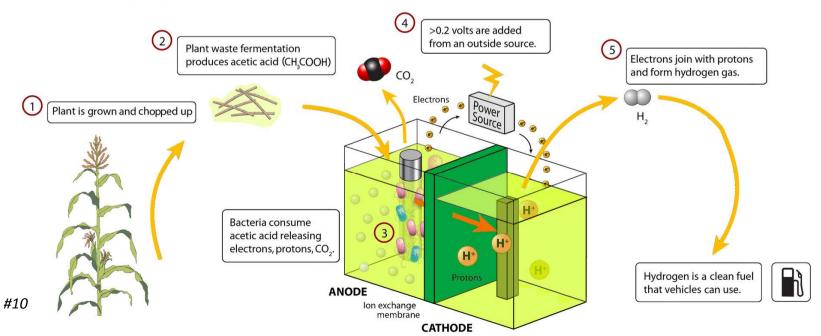
- Generation of energy out of bio-waste / organic matter
- Direct conversion of substrate energy to electricity
- No gas treatment required
- Aeration may not be needed (the cathode may be passively aerated)

Disadvantages

- Low power density: losses of electric potential significant
- High initial cost

Microbial electrolysis cell (MEC)

- Not an electricity-generating, but electricity-consuming process to produce hydrogen or methane as a fuel
- Hydrogen is produced by reducing protons at the cathode
 - The voltage required to reduce protons is provided by: substrate utilization by microorganisms at the anode + additional voltage supply from an outside source



References

- #1) Isaka, K., Kimura, Y., Matsuura, M., Osaka, T., Tsuneda, S. (2017) First full-scale nitritation-anammox plant using gel entrapment technology for ammonia plant effluent. Biochemical Engineering Journal, 112: 115-122.
- #2) Scherson, Y. D., Wells, G. F., Woo, S. -G., Lee, J., Park, J., Cantwell, B. J., Criddle, C. S. (2013) Nitrogen removal with energy recovery through N_2O decomposition. Energy & Environmental Science, 6(1): 241-248.
- #3) https://en.wikipedia.org/wiki/Aerobic_granulation
- #4) Gogina, E., Gulshin, I. Simultaneous nitrification and denitrification with low dissolved oxygen level and C/N ratio. Procedia Engineering, 153: 189-194.
- #5) https://www.dutchwatersector.com/news/nereda-waste-water-technology-proves-40-energy-saving-atwwtp-epe-the-netherlands
- #6) https://www.dutchwatersector.com/news/water-board-noorderzijlvest-commissioned-second-dutch-nereda-plant-at-wwtp-garmerwolde
- #7) Rabaey, K., Verstraete, W. (2005) Microbial fuel cells: novel biotechnology for energy generation. Trends in Biotechnology, 23(6): 291-298.
- #8) https://wou.edu/chemistry/courses/online-chemistry-textbooks/ch450-and-ch451-biochemistry-defining-life-at-the-molecular-level/chapter-2-protein-structure/
- #9) Simeon, M. I., Raji, O. A., Gbabo, A., Okoro-Shekwaga, C. A. (2016) Performance of a single chamber soil microbial fuel cell at varied external resistances for electric power generation. Journal of Renewable Energy and Environment, 3(3): 53-58.
- #10) https://en.wikipedia.org/wiki/Microbial_electrolysis_cell