Maximizing Microorganism-Based Energy Resources from Used Water

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I ❤

Activated Sludge!
Activated Sludge Can Do Many Things!

- BOD Removal
- Nitrification
- Total N Removal
- Biodegradation of Micropollutants
- Total P Removal
And, it has so many “fun” challenges

- Sludge Bulking
- Deflocculation
- Odors
- Loss of nitrification
- Poor O$_2$ Transfer
- Excessive Sludge
- Recalcitrant Organics
The **Problem** is that Activated Sludge is a..........
Giant Energy Consumer

Big Generator of Waste Biosolids

Huge Economic Burden

Significant Source of Greenhouse Gases
But, wastewaters have a lot of valuable resources……

that Activated Sludge “tosses away” while incurring huge costs
So, let’s congratulate ourselves for Activated Sludge and…

graduate to making “wastewater” the resource it is.

Resources Reborn!
Multiple Major Resources

- Energy – in the BOD
- Nutrients – the P and N
- Clean Water

Enhancing environmental and economic value propositions
Multiple Major Resources

- Energy – in the BOD
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Enhancing environmental and economic value propositions
Energy- and P-rebirth Strategy

Sources

- High P and BOD (animal waste) (40% of mined P)
- Medium P and BOD (sewage) (16% of mined P)
- Low P and BOD (runoff) (46% of mined P)

Conversions

- Convert Org-P to Inorg-P simultaneously with anaerobic bioenergy production
- Convert Org-P to Inorg-P with an AOP

Recovery and Use

- Energy output, e.g., CH$_4$ or H$_2$
- Separate, concentrate, and recover Inorganic-P
- Water for reuse
- Recovered P for food crops or other uses
What has been the holdup with methanogenesis?

- Slow-growing methanogens
  - Need excellent biomass retention
- Inadequate effluent quality for BOD
- Dissolved CH$_4$
  - Loss of CH$_4$ energy
  - Greenhouse gas emission
- Sulfate reduction
  - Odors and loss of CH$_4$ energy
- Minimal N and P removals
Anaerobic Membrane Bioreactor (AnMBR) – commercially ready

Conceptually, a linking of an anaerobic digester with a membrane separator to effect perfect solids retention for a long SRT and high enough biomass concentration.

Or, just immerse the membranes in the anaerobic reactor to simplify
Good effluent quality, modest HRT, managed TMP

Skyway WWTP Pilot
Burlington, Ontario

Temperature – 22 °C

Influent:
COD – 224 mg/l
BOD$_5$ – 93 mg/l

Effluent:
COD – 47 mg/L
BOD$_5$ – 14 mg/L

HRT – 7.5 h
Methane can be recovered from the effluent*

Methane removal vs. water flow rate at 12 °C
55 mm Hg absolute vacuum
Inlet CH₄ of 22 mg/L

Methane Removal, %

Water Flow Rate, m³/d

Industrial Gas Transfer Contactor

Vacuum pump energy requirement ~ 0.02 kWh/m³

*Demonstrated

* Can be >20% of influent COD!
Staged Anaerobic Fluidized MBR (SAF-MBR)

12 m³/day AFMBR Pilot Plant To Treat Bucheon, South Korea, Primary Effluent
• **Wastewater characteristics**
  - COD  
    \[ 300 \pm 60 \text{ mg/L} \]
  - BOD\(_5\)  
    \[ 160 \pm 45 \text{ mg/L} \]

• **Hydraulic Retention Time**
  - AFBR  
    2 hours
  - AFMBR  
    2.6 to 4.8 hours
  - Total  
    4.6 to 6.8 hours
SAF-MBR Effluent BOD$_5$ – Temp was 8 – 32°C

USA EPA Upper Limit

Shin et al., Bioresource Technology, 159, 95-103 (2014)
**COD Mass Balance**

- 36% Dissolved Methane
- 10% Permeate
- 9% Unknown
- 11% Biosolids Wasting
- 11% Sulfate Reduction
- 23% Gaseous Methane
A Microbial Fuel Cell, or MFC

Microbial Electrochemical Cells (MXCs)

- Bacteria living as a biofilm on an electrode remove electrons from an organic fuel and transfer them to the electrode and through the circuit to harvest electrical energy, or bio-power.

- Thus, fuel-cell technology can use renewable organic fuels from wastes and fuel crops.

- The technology is still in the research stage, but we are beginning to scale up.
The reaction potential drives all biological, chemical, and electrochemical processes in MFC => typical recovered potentials are 0.3 - 0.6 V
Modifying the MXC to an MEC to Produce H₂

e⁻ donor half reaction: \( \text{CH}_3\text{COO}^- + 3 \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{HCO}_3^- + 8\text{H}^+ + 8\text{e}^- \) - 0.29 V

e⁻ acceptor half reaction: \( 8\text{H}^+ + 8\text{e}^- \rightarrow 4 \text{H}_2 \) - 0.41 V

Net reaction: \( \text{CH}_3\text{COO}^- + 3\text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{HCO}_3^- + 4 \text{H}_2 \) - 0.12 V

In a **Microbial Electrolysis Cell (MEC)**, we exclude O₂ and add power (applied voltage) to have a low enough cathode potential to produce H₂.
Modifying the MXC to an MPC to Produce H$_2$O$_2$ (peroxide)

$\text{e}^-$ donor half reaction: 
$\text{CH}_3\text{COO}^- + 3 \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{HCO}_3^- + 8\text{H}^+ + 8\text{e}^- \quad -0.29 \text{ V}$

$\text{e}^-$ acceptor half reaction:
$8\text{H}^+ + 8\text{e}^- + 8\text{O}_2 \rightarrow 4 \text{H}_2\text{O}_2 \quad 0.31 \text{ V}$

Net reaction:
$\text{CH}_3\text{COO}^- + 3\text{H}_2\text{O} + 8\text{O}_2 \rightarrow \text{CO}_2 + \text{HCO}_3^- + 4 \text{H}_2\text{O}_2 \quad 0.6 \text{ V}$

In a Microbial Peroxide Cell (MPC), we use only a C-based cathode to get to reduce O$_2$ only to H$_2$O$_2$. This provides only a small power output, but generates a valuable oxidant and disinfectant.
Anode Respiring Bacteria (ARB)

\[
\text{CH}_3\text{COOH} + 3\text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{HCO}_3^- + 8\text{H}^+ + 8\text{e}^- 
\]

- Specialized bacteria capable of transferring electrons to a solid anode.
  - Must carry “extracellular electron transfer” (EET)
  - Form a biofilm in the anode surface

- In order to have a feasible MXC system, ARB must:
  - Consume the desired substrates
  - Produce high current densities
  - Minimize energy losses
Processes that can limit current production

Substrate + H₂O → CO₂ + 8H⁺ + 8e⁻

1. Catalyst (ARB) for substrate oxidation
2. Substrate diffusion
3. e⁻ transport (potential driven)
4. H⁺ transport (pH and buffering)
Mechanisms with Anode-Respiring Bacteria (ARB)

\[ \text{C}_2\text{H}_4\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \]

1. Catalyst (ARB) for substrate oxidation
2. Substrate (C\textsubscript{2}H\textsubscript{4}O\textsubscript{2}) supply by diffusion
3. e\textsuperscript{-} transport (potential driven) by conduction
4. H\textsuperscript{+} transport (pH control) by diffusion
Anode-respiring bacteria (ARB) are able to oxidize organic substrates at a higher rate than most other biofilm processes. This is due to their efficient extracellular electron transport, which yields no electron-acceptor limitations. For example, much faster than aerobic respiration!
Status and prospect for MXCs -- Constraints

• The true rate-constraining mechanisms are
  ✦ $H^+$ transfer out of the biofilm by diffusion
  ✦ Hydrolysis of complex organic solids

• The design of MXCs requires a full understanding of microbiological and electrochemical processes.
  ✦ Minimize voltage losses at the cathode.
  ✦ Avoid electron-losing processes, such as methanogenesis or oxygen leakage.
To have a favorable value proposition:

- Low-cost materials
- Compact designs
- Modular designs for ready scalability
- Multiple high-value outputs, tailored to client needs
  - For example, the economic value of H₂ is about 5 times greater than CH₄ on an e⁻ (or BOD) basis!
H₂ from an MEC or CH₄?

• H₂ can be used to power chemical fuel cells, say to drive your car of the future.

• H₂ is a major feedstock to the chemical industry for reductions, or hydrogenations.

• H₂ can be used for water-pollution control to reduce oxidized contaminants, like nitrate, perchlorate, selenate, and TCE ➔ The MBfR technology.

• The economic value of H₂ is about 5 times greater than CH₄ on an e⁻ (or BOD) basis!
Take-home Lessons

Activated sludge is good for “treatment,” but we need to move to “resource.”

No longer wastes, but

Resources Reborn!
Take-home Lessons

We can convert the BOD to \( \text{CH}_4 \) or electrical power or \( \text{H}_2 \) or \( \text{H}_2\text{O}_2 \)

- Methanogenesis is possible now with AnMBRs and SAF-MBRs
- MFCs for electrical power, MECs for \( \text{H}_2 \), and MPCs for \( \text{H}_2\text{O}_2 \) are still some years away from commercial success, but research and development advances are coming rapidly.
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