Demonstration and Commercialization of ARoNite™, A Novel Hydrogen-based Membrane Biofilm Biological Reduction Process

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Ryan Overstreet, APTwater
Dr. Bruce Rittmann, Arizona State University
The use of naturally-occurring biological mechanisms in an engineered system to accomplish a water treatment goal

- **Aerobic systems (oxidation)**
  - Removal of biodegradable organics for TOC reduction
  - Examples: Riverbank filtration, unchlorinated media filters

- **Anaerobic/anoxic systems (reduction)**
  - Removal of “oxyanions” and halogenated compounds
    - Nitrate, chromate (hexavalent chromium), perchlorate, selenate (selenium), DBCP, TCE, PCE, TCP….

- **If it’s natural, why is it “new?”**
  - A growing realization that not all bacteria are bad
Denitrification is a dissimilatory biological process that sequentially reduces $\text{NO}_3^-$ to $\text{N}_2$ (a 5-electron reduction).

\[
\text{NO}_3^- + 2e^- \rightarrow \text{NO}_2^- \\
\quad + e^- \rightarrow \text{NO} \\
\quad + e^- \rightarrow 0.5\text{N}_2\text{O} \\
\quad + e^- \rightarrow 0.5\text{N}_2
\]

We chose $\text{H}_2$ gas as the electron donor

\[
\text{H}_2 \rightarrow 2\text{H}^+ + 2e^- \\
\text{(2 electrons per $\text{H}_2$ molecule)}
\]
What are the proper conditions?

- Anoxia, or dissolved oxygen removed
- Excellent biomass retention, usually as a biofilm
- Satisfactory pH, near neutral
- Availability of nutrients, particularly P
- Sufficient electron donor
  - Organic compound (for heterotrophs)
  - Hydrogen gas (H₂) (for autotrophs)
Why Bacterial Reduction Using Hydrogen?

Major advantages over organic e⁻ donors (heterotrophic)

- H₂ supports autotrophic bacteria, which use bicarbonate as their Carbon source; thus, no organic Carbon source must be added.
- Relatively low-cost electron donor that is commercially available as a bulk chemical or can be generated on-site.
- No dosing challenge, easy to control
- Non-toxic, no residual
- Low biomass yield, producing less biomass that must be wasted.
- Based on growing microbiology research, H₂ should be available as donor for virtually all oxidized contaminants.
A novel *natural partnership* between technology and biofilms.

For the first time, we can deliver $\text{H}_2$ to microorganisms as the electron donor in a safe and efficient manner.

- Gaining all those advantages discussed in previous slide!
ARoNite (MBfR) Brief History

- Membrane Biofilm Reactor Concept - ~ 1996 – by Dr. Bruce Rittmann & Dr. K-C Lee
- Demonstration for denitrification (late 1990s) – Dr. Rittmann & Dr. Lee
- First publication (2000); now > 40 publications
- Demonstration for perchlorate reduction (early 2000s) -- Dr. Rittmann & Dr. Lee
- Field demonstration (early 2000s) – w/ MWH
- First patent (2002)
- APTwater licenses the technology and partners (2004)
- Since 2005 APTwater has been expanding the scope of oxidized contaminants, conducting field testing, developing commercial system
- The concept was awarded the 2011 Environmental Engineering Excellence Award from the American Academy of Environmental Engineers!
- ARoNite received NSF 61 certification in Dec 2011
- The first commercial ARoNite system went on line in Jan 2012
- CDPH testing and review - 2012
- **ARoNite will be the one of the first permitted and operating biological reduction process in the US for drinking water treatment**
What does ARoNite stand for?

**ARo Technologies** –

Autotrophic — an organism capable of making organic molecules from inorganic sources. Examples are plants, algae, some bacteria

Reduction — Chemical reaction in which an electron is gained

of - Nitrates, Chromium, Selenium and other compounds

Targeting Autotrophic Reduction of Nitrates to innocuous compounds, using hydrogen, carbon dioxide and electricity as consumables.

In pilot and field testing are:

• **ARoChrome** targeting Cr\(^{6+}\) in water supplies
• **ARoPerc** targeting specific chlorinated compounds in water i.e. ClO4

In Development:

• **ARoSel** targeting Selenium, naturally occurring and from flue gas desulfurization, oil production and refining
Hydrogen is either generated or delivered on site.

Carbon Dioxide is delivered on site and used to control pH.

Carbon Dioxide & Hydrogen are fed to the ARoNite Reactor creating the optimum environment for the biofilm.

Contaminated water is fed to the ARo Reactor allowing the biofilm to grow and reduce the target contaminant from the water.

Treated water is filtered and disinfected using conventional technologies before discharge to distribution system.
Biofilm supported on a bubble-less gas-transfer fiber

Biofilm consumes \( \text{H}_2 \) on demand from hollow fiber surface, driving more diffusion

Water

\( \text{O}_2, \text{NO}_3^-, \text{ClO}_4^- \)

Polypropylene Hollow Fiber Membrane

100-300 \( \mu \text{m} \)
How the ARoNite Reactor Works

• Naturally occurring biology grows on the surface of a gas diffusion membrane sheet woven of a proprietary hollow fibers

• Several of these sheets are spiral wound around a water feed tube with a water channel spaced between the sheets

• Hydrogen and Carbon Dioxide are fed to the lumen of the hollow fibers

• Water passes between the sheets making contact with the biofilm

• Nitrates are reduced to Nitrogen and Water

• Over time, cells fall off into water and are filtered

• Automated purge cycle prevents fouling
What does ARo Technologies stand for?
<table>
<thead>
<tr>
<th>Location</th>
<th>Contaminant</th>
<th>Dates</th>
<th>System configuration</th>
<th>Significant Outcome</th>
</tr>
</thead>
<tbody>
<tr>
<td>La Puente, CA</td>
<td>Groundwater ClO$_4^-$</td>
<td>~2003</td>
<td>Pilot module</td>
<td>AwwaRF Report by MWH, early system design info.</td>
</tr>
<tr>
<td>Modesto (Grayson)</td>
<td>Groundwater NO$_3^-$</td>
<td>9/06 – 6/11</td>
<td>Pilot module</td>
<td>Multiple fiber and module construction improvements, CDPH data collected</td>
</tr>
<tr>
<td>Lake Arrowhead</td>
<td>Tertiary effluent NO$_3^-$</td>
<td>3/07-11/07</td>
<td>Pilot module</td>
<td>WateReuse Report by Trussell</td>
</tr>
<tr>
<td>San Bernardino</td>
<td>Groundwater NO$_3^-$, ClO$_4^-$</td>
<td>3/08 - 1/09</td>
<td>Pilot module</td>
<td>Flow maldistribution limit performance, ESTCP with CDM reauthorized</td>
</tr>
<tr>
<td>Glendale, AZ</td>
<td>Groundwater NO$_3^-$</td>
<td>4/08 - 2/09</td>
<td>Pilot module</td>
<td>WRF Report by CH2MHIll, positive comparison to IX and heterotrophic systems</td>
</tr>
<tr>
<td>Rancho Cordova</td>
<td>Groundwater ClO$_4^-$</td>
<td>9/08 – 11/10</td>
<td>Pilot module</td>
<td>Successfully treat 14 ppm to &lt;4 ppb</td>
</tr>
<tr>
<td>Rancho Cordova</td>
<td>Groundwater ClO$_4^-$</td>
<td>10/08 – 11/10</td>
<td>Commercial module</td>
<td>Develop and test larger modules</td>
</tr>
<tr>
<td>Ojai, CA</td>
<td>Tertiary effluent NO$_3^-$</td>
<td>2/10 – 12/10</td>
<td>Commercial module</td>
<td>Tested multitude of large modules in one system</td>
</tr>
<tr>
<td>Rialto, CA</td>
<td>Groundwater NO$_3^-$, ClO$_4^-$</td>
<td>5/11 – 2/12</td>
<td>Commercial module</td>
<td>ESTCP project with CDM based on improvements in commercial module</td>
</tr>
<tr>
<td>Burbank, CA</td>
<td>Groundwater NO$_3^-$, Cr(VI)</td>
<td>6/11 - 11/12</td>
<td>Commercial module</td>
<td>Tested low ppb Cr(VI) removal</td>
</tr>
<tr>
<td>Rancho Cucamonga</td>
<td>Groundwater NO$_3^-$</td>
<td>11/11 - current</td>
<td>Commercial module</td>
<td>1st commercial, approved and operating system for biological nitrate removal</td>
</tr>
</tbody>
</table>
**ARoNite Case Study: City of Modesto**

- Sampling and analysis protocol developed w/CDPH for continuous 30-day test
- October 29, 2008, to December 1, 2008
- Positive results on all analyses – met DW standards

<table>
<thead>
<tr>
<th>Analyte averages</th>
<th>Inlet</th>
<th>Final Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrate-N (mgN/L)</td>
<td>14.1</td>
<td>0.3</td>
</tr>
<tr>
<td>Nitrite-N (mgN/L)</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Chromium (μg/L)</td>
<td>18.3</td>
<td>3.5</td>
</tr>
<tr>
<td>Selenium (μg/L)</td>
<td>10.5</td>
<td>6.5</td>
</tr>
<tr>
<td>Copper (μg/L)</td>
<td>9.5</td>
<td>&lt;2</td>
</tr>
</tbody>
</table>
• All DW requirements met
  – APTwater encouraged to apply for operating permit on a specific treatment system for approval

• Nitrate Conditional Acceptance of the treatment technology via Cucamonga Valley Water District project with supporting data from Modesto (Grayson) pilot

• Operating Permit approval – at a specific site

• Key CDPH requirements for post-treatment after any biological treatment process are:
  – Turbidity <0.3 NTU
  – Disinfection to 4-log virus deactivation/removal
ARoNite Installation Cucamonga Valley Water District

Project Details:

Drinking Water Well #23
Water-by-the-Gallon (DBOOM) Denitrification

- CVWD has 12 wells shut down out of 30 for nitrates
- All high in nitrate, well over MCL
- Target allowed nitrate <31 ppm
- Two step contract
  - Step 1: Start up and run 125 gpm
  - Step 2: Expand plant to 650 gpm
- Plant construction; Aug-October, started up Nov 2011
- CDPH testing protocols defined and completed
Show Consistent Treatment to produce Potable Water

Nitrate Removal (1 mg-N/L or 4.5 mg/L) and Nitrite (< 0.5 mg-N/L)
Turbidity (<0.3 NTU)
Disinfection (Residual Chlorine >0.3 and < 2.0 mg/L)
  e. coli < 2.2 MPN/100 ml
  HPC < 500 cfu/ml
pH ≥ 6.5 and ≤ 8.5
Aeration – Restore Dissolved Oxygen
THM Formation Potential < 64 µg/L (80% of MCL)
HAA5 Formation Potential < 48 µg/L (80% of MCL)

Reliability ≥ 95% uptime
ARoNite Process Overview and Monitoring Points

Well 23 → ARo-Nite → Aeration → Filtration → Disinfection Tank

- **Micro Nutrients**
- **Process Nitrate analyzer to monitor several points within process**
- **Compliance Turbidity analyzer**
- **Compliance Nitrate analyzer**

**Flow Diagram:**

- **H₂, CO₂, Air**
- **Backwash Water**
- **Sanitary Sewer**
- **NaOCl**
- **Cl₂ analyzer**
- **Reservoir #3**

**Compliance:**

- **Nitrate analyzer**
- **Turbidity analyzer**
- **Cl₂ analyzer**
Project Time Line:

• System Installation Started September 2011
• System Installation Completed November 2011
• System startup and inoculation November to Jan. 2012
• 30 Day Demonstration Started January 25, 2012
• 30 Day Demonstration Completed on February 24, 2012
• Challenge Tests – March 2012
• Extended Demonstration Testing – October and December 2012

During Demonstration

• 187 Field Analysis conducted each week
• On-line Measurements taken every minute
• 137 Lab Analysis Taken and Analyzed each week.
## Analyses Conducted

### OFF-SITE LAB

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrate-N</td>
<td></td>
</tr>
<tr>
<td>Nitrite-N</td>
<td></td>
</tr>
<tr>
<td>Ammonia (mg/L)</td>
<td></td>
</tr>
<tr>
<td>TKN (mg/L)</td>
<td></td>
</tr>
<tr>
<td>Perchlorate (µg/L)</td>
<td></td>
</tr>
<tr>
<td>Sulfate (mg/L)</td>
<td></td>
</tr>
<tr>
<td>Sulfide (mg/L)</td>
<td></td>
</tr>
<tr>
<td>Total Phosphorus as P (mg/L)</td>
<td></td>
</tr>
<tr>
<td>Alkalinity Group in CaCO3 units</td>
<td></td>
</tr>
<tr>
<td>Calcium (mg/L)</td>
<td></td>
</tr>
<tr>
<td>Iron (mg/L)</td>
<td></td>
</tr>
<tr>
<td>Magnesium (µg/L)</td>
<td></td>
</tr>
<tr>
<td>Potassium (mg/L)</td>
<td></td>
</tr>
<tr>
<td>Sodium (mg/L)</td>
<td></td>
</tr>
<tr>
<td>Heavy Metals</td>
<td></td>
</tr>
<tr>
<td>TOC (mg/L)</td>
<td></td>
</tr>
<tr>
<td>DOC (mg/L)</td>
<td></td>
</tr>
<tr>
<td>Heterotrophic Plate Counts (CFU/ml)</td>
<td>Total Coliform</td>
</tr>
<tr>
<td></td>
<td>e.Coli (MPN/100 ml)</td>
</tr>
<tr>
<td></td>
<td>TSS (mg/L)</td>
</tr>
<tr>
<td></td>
<td>TDS</td>
</tr>
<tr>
<td></td>
<td>Total Settleable Solids</td>
</tr>
<tr>
<td></td>
<td>Turbidity (NTU)</td>
</tr>
<tr>
<td></td>
<td>pH</td>
</tr>
<tr>
<td></td>
<td>THM (µg/L)</td>
</tr>
<tr>
<td></td>
<td>THMFP (µg/L)</td>
</tr>
<tr>
<td></td>
<td>HAA (µg/L)</td>
</tr>
<tr>
<td></td>
<td>HAAFP (µg/L)</td>
</tr>
<tr>
<td></td>
<td>VOC</td>
</tr>
<tr>
<td></td>
<td>Total Chlorine Residual</td>
</tr>
<tr>
<td></td>
<td>Chlorine Demand</td>
</tr>
</tbody>
</table>

### FIELD AND ONLINE

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrate-N Field</td>
<td></td>
</tr>
<tr>
<td>Nitrite-N Field</td>
<td></td>
</tr>
<tr>
<td>ARoNite (N as NOx)</td>
<td></td>
</tr>
<tr>
<td>ARoNite Turbidity</td>
<td></td>
</tr>
<tr>
<td>Dissolve Oxygen (DO) - Field</td>
<td></td>
</tr>
<tr>
<td>Temperature - Field °C</td>
<td></td>
</tr>
<tr>
<td>pH - Field</td>
<td></td>
</tr>
<tr>
<td>ARoNite pH</td>
<td></td>
</tr>
<tr>
<td>ARoNite Residual Chlorine Field</td>
<td></td>
</tr>
</tbody>
</table>

**Note:** Some fields may be excluded due to space limitations.
Nitrate as NO3 Influent v. Effluent - Rancho

Note values are as Nitrate, not N

MCL – 45 as nitrate, 10 as N

Product below 1 mg N/L (4.5 as nitrate)
Comparison Summary – Lab, On-Line and Field

- Good agreement of online nitrate sensor with lab data (IC)
- Poor agreement of field nitrate analyses (Hach Cd-reduction colorimeter) with lab and online data, variable results on same sample
- Good agreement field (Hach colorimeter) and lab nitrite
- Good agreement online, field, lab turbidity – after air bubble trap installed
- Good agreement online, field, lab chlorine residual

(Online instruments – all from Endress+Hauser)
## Disinfection Final Product

<table>
<thead>
<tr>
<th>Location</th>
<th>e. coli</th>
<th>HPC (CFU/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MPN/100 ml</td>
<td>Average</td>
</tr>
<tr>
<td>SP1 Raw ¹</td>
<td>&lt;1.1</td>
<td>45</td>
</tr>
<tr>
<td>SP3 Aeration Effluent ²</td>
<td>&lt;1.1</td>
<td>&gt;5,700</td>
</tr>
<tr>
<td>SP4 Filtration Effluent ²</td>
<td>&lt;1.1</td>
<td>2875</td>
</tr>
<tr>
<td>SP5 Final Effluent ²</td>
<td>&lt;1.1</td>
<td>9</td>
</tr>
<tr>
<td>SP6 Backwash Effluent ¹</td>
<td>&lt;1.1</td>
<td>&gt;5,700</td>
</tr>
</tbody>
</table>

¹ 5 Samples Taken  
² 8 Samples Taken
### TOC, DOC and BDOC Results

<table>
<thead>
<tr>
<th>Location</th>
<th>DOC (mg/L)</th>
<th>TOC (mg/L)</th>
<th>BDOC (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>SP1 Raw</td>
<td>0.34</td>
<td>0.43</td>
<td>0.30</td>
</tr>
<tr>
<td>SP2 Lag Effluent</td>
<td>0.57</td>
<td>0.69</td>
<td>0.45</td>
</tr>
<tr>
<td>SP3 Aeration Effluent</td>
<td>0.60</td>
<td>0.74</td>
<td>0.46</td>
</tr>
<tr>
<td>SP4 Filtration Effluent</td>
<td>0.52</td>
<td>0.63</td>
<td>0.37</td>
</tr>
<tr>
<td>SP5 Final Effluent</td>
<td>0.56</td>
<td>0.65</td>
<td>0.47</td>
</tr>
</tbody>
</table>

1 5 Samples Taken

2 BDOC results are the difference between an initial and final DOC, both positive and negative values used in summary statistics

- Approximately 0.2 mg/L increase in DOC/TOC across treatment train, consistent with Modesto/Grayson and other pilot data – from soluble microbial products (SMP).
- BDOC data highly variable and not consistent with BDOC being a subset of DOC, which is a subset of TOC.
## Disinfection By-Products Initial/Product Comparison

### THM (µg/L) and THM Formation Potential (µg/L)\(^1\)

<table>
<thead>
<tr>
<th>Location</th>
<th>THM (µg/L)</th>
<th>THM Formation Potential (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Location</td>
<td>Average</td>
</tr>
<tr>
<td>SP1 Raw</td>
<td></td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>SP5 Final Effluent</td>
<td></td>
<td>2.2</td>
</tr>
</tbody>
</table>

\(^1\) 5 Samples Taken

### HAA\(_5\) (µg/L) and HAA\(_5\) Formation Potential (µg/L)\(^1\)

<table>
<thead>
<tr>
<th>Location</th>
<th>HAA(_5) (µg/L)</th>
<th>HAA(_5) Formation Potential (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Location</td>
<td>Average</td>
</tr>
<tr>
<td>SP1 Raw</td>
<td></td>
<td>&lt;2</td>
</tr>
<tr>
<td>SP5 Final Effluent</td>
<td></td>
<td>&lt;2</td>
</tr>
</tbody>
</table>

\(^1\) 5 Samples Taken
\(^2\) 2 Samples Taken
Challenge Tests Results:

- 1-hour H2 off, continue water feeding
- 1-hour power suddenly off
- 24-hour power suddenly off

➤ All had instant nitrate reduction and back to normal after two hydraulic residence times

- 10-day “well outage”
  - Kept system “alive” on dissolved oxygen, recycled aerated water

➤ Instant nitrate reduction, approximately 5HRT back to normal
Miscellaneous Data

• One detection of Perchlorate at 4.5 µg/L in the Raw water, ND in Final Product
• One detection of Total Cr at 3 µg/L in the Raw water on Day 1, ND in Final Product
• One detection of Cu at 2.3 µg/L in Filtrate on Day 1, ND in Final Product
• Manganese was detected in the Raw Water 2.2 µg/L, ND in Final Product
• Dissolved Oxygen in Final Product averaged 6.6 ± 0.8 mg/L (Raw Water Ave. DO = 8.7)
• Temperature of the Final Product averaged 72.4 ± 1.3°F (Raw Water Temp 68.4±1.2)

All other Water Quality parameters were unchanged
First Demonstration Outcome

- Nitrate removal to target - the “easy part”
- CDPH requested below improvements and then a second, less extensive demonstration
  - Process control – lack of tuning – Fixed
  - Filtration system – easily upset, inconsistent performance
  - Residual chlorine control – Fixed, improved flow-paced dosing
Filtration System Improvements

- Filtration system – easily upset, inconsistent performance
  - Entrained air in filter feed, bubble traps before turbidimeter
  - Dose filter aid farther upstream (not enough mix/coag time)
  - Jar and filter testing with alternate coagulants (found ACH/polymer best)
  - Discovered leaking o-rings in filter valves (Kinetico Hydrus)

Underside of top filter valve

- O-ring to seal internal riser pipe
- 2/3rd of o-ring groove
  (Not supposed to be loose)
So, now what....

- System mothballed to await regulatory approval.
- CDPH Water Treatment Committee reviewed and issued Conditional Acceptance Letter 7/26/13.
- Now installing filtration improvements to restart system.
- Then will apply to local CDPH district for operating permit.
What to walk away with

• Utilizes naturally-occurring indigenous bacteria - no seeding required
• Very low biomass compared to carbon based system
• Adds no organic residual, no dosing challenges
• Self regulated demand of hydrogen
• Hydrogen can be generated on-site as needed
• Meets and exceeds state and federal drinking water standards for drinking water
• NSF-61 certified
• California DPH approval for drinking water applications
• No brine or concentrated waste as Nitrate is destroyed versus concentrated
• Remote monitoring, troubleshooting and control of equipment
Acknowledgements

**CVWD**: Rob Hills, Ed Diggs, J.R. Rivas, operations team

**CDM Smith**: Dave Cary, Jesse Aguilar, Luis Leon

**APTwater**: Steve Gagnon, Rich Buday, Ryan Overstreet, Reid Bowman

**ASU**: Bruce E. Rittmann, Aura Ontiveros-Valencia, He-Ping Zhang, Youneng Tang, Bi-O Kim

Thanks for your Time and Interest

David Friese, P.E.

dfriese@aptwater.com
ARo system installed, no post aeration and filtration steps
- Ran 205 days on unspiked feed
- Began Cr(VI) spike to feed, ran 248 days
- No use of coagulant/filtration steps that could remove additional Cr(III)

### Analyte Inlet Final Product

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Inlet</th>
<th>Final Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrate-N (mgN/L)</td>
<td>8-9</td>
<td>&lt;0.3</td>
</tr>
<tr>
<td>Chromium(VI) (μg/L)</td>
<td>4-6</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Chromium total (μg/L)</td>
<td>4-6</td>
<td>3-4</td>
</tr>
<tr>
<td>Spiked Cr(VI) (μg/L)</td>
<td>15-25</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Chromium total (μg/L)</td>
<td>15-25</td>
<td>7-12</td>
</tr>
<tr>
<td>Spiked Cr(VI) (μg/L)</td>
<td>40-50</td>
<td>&lt;2</td>
</tr>
<tr>
<td>Chromium total (μg/L)</td>
<td>40-50</td>
<td>15-20</td>
</tr>
</tbody>
</table>
Peer-reviewed publications (MBfR in academia)


