Combined Ion Exchange for Removal of Dissolved Organic Carbon and Hardness

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Removal of Multiple Contaminants: Biological Treatment and Ion Exchange
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Cedar Key Water & Sewer District
Challenges faced by small water systems


- Management and operations
- Source water
- Security
- Pumps
- Compliance
- Data verification
- Treatment
- Finished water storage
- Distribution
- Financial
Challenges faced by small water systems

- Fe oxidation
- DOC removal
- Hardness removal
- Turbidity removal
- Disinfection
Challenges faced by small water systems

- Fe oxidation
- DOC removal
- Hardness removal
- Turbidity removal
- Disinfection

Combined ion exchange (CIX)
Ion exchange

Microscale

Anion exchange resin

Mobile counterion

Cl⁻

Cl⁻

Cl⁻

Cl⁻

Cl⁻

X⁻

Contaminant ion

Macroscale

Contaminant

Contaminant-free
Regeneration

NaCl

NaCl + contaminants
Combined ion exchange (CIX)
CIX: DOC and hardness removal
CIX & multi-contaminant removal
Ion exchange reactors

- Fixed bed reactor
- Completely mixed reactor with resin recycle
Proof of concept

Proof of concept

Experimental design

• Groundwater from Cedar Key
  • DOC: 5.6 mg/L
  • Hardness: 275 mg/L as CaCO$_3$
• Anion exchange resin: 2 mL/L MIEX-Cl
• Cation exchange resin: 16 mL/L MIEX-Na
• Single-loading jar tests
  • Simultaneous: MIEX-Cl + MIEX-Na
  • Sequence 1: MIEX-Cl → MIEX-Na
  • Sequence 2: MIEX-Na → MIEX-Cl
• NaCl regeneration
• 70% DOC removal and 55% hardness removal

## Proof of concept

<table>
<thead>
<tr>
<th>Parameter</th>
<th>MIEX-Cl + MIEX-Na</th>
<th>Finished drinking water&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.7</td>
<td>8.1</td>
</tr>
<tr>
<td>DOC (mg C/L)</td>
<td>1.7</td>
<td>1.1</td>
</tr>
<tr>
<td>Hardness (mg/L as CaCO&lt;sub&gt;3&lt;/sub&gt;)</td>
<td>112</td>
<td>173</td>
</tr>
<tr>
<td>Chloride (mg/L)</td>
<td>49</td>
<td>60</td>
</tr>
<tr>
<td>Sulfate (mg/L)</td>
<td>3.1</td>
<td>1.1</td>
</tr>
</tbody>
</table>

<sup>a</sup> Cedar Key Water & Sewer District; August 2009.
Proof of concept

- Decrease in hardness removal and increase in DOC removal after 3 regeneration cycles
- Simultaneous and sequential ion exchange showed similar removals after 3 regeneration cycles

Proof of concept

Conclusions

• MIEX-Cl and MIEX-Na can be used in a single completely mixed vessel to simultaneously remove DOC and hardness
• MIEX-DOC and MIEX-Ca can be effectively regenerated using NaCl in a single completely mixed vessel
• Simultaneous and sequential ion exchange showed approximately equal removal after three regeneration cycles
• NaCl regeneration solution prepared using tap water (i.e., containing hardness and alkalinity) provided the same regeneration efficiency as NaCl regeneration solution prepared using hardness-free, deionized water
Proof of concept

Observations

- MIEX-Na removed DOC in addition to hardness. This was unexpected because DOC is negatively charged.
- Combined ion exchange is expected to be an effective pretreatment to reduce membrane fouling, i.e., decrease organic fouling by DOC and inorganic scaling by calcium minerals.
Focus on cation exchange

Focus on cation exchange

Experimental design

- Synthetic water to mimic Cedar Key groundwater
  - Suwannee River NOM (~5 mg/L DOC)
  - Hardness as $\text{Ca}^{2+}$, $\text{Mg}^{2+}$, and $\text{Ca}^{2+}/\text{Mg}^{2+}$ (~250 mg/L as $\text{CaCO}_3$)
- Cation exchange resin
  - 16 mL/L MIEX-Na
  - 3.1 mL/L Purolite C106-Na
  - Resin-Na, -Ca, -Mg, -Sr, and -Ba
- Batch equilibrium experiments
Focus on cation exchange

- DOC removal by magnetic cation exchange resin
- No DOC removal by non-magnetic cation exchange resin

Combined ion exchange, revisited

- Combined ion exchange is additive

Indarawis & Boyer, 2013. *Separation and Purification Technology*
Focus on cation exchange

Conclusions

• DOC removal was approximately 20% for MIEX-Na resin with no hardness cations in solution
• DOC removal by MIEX resin increased when the presaturant ion was a divalent metal cation or divalent metal cation was present in solution or both
• There was no measureable DOC removal by the non-magnetic cation exchange resin for all conditions of presaturant ion and metal cations in solution, with the exception of barium as the presaturant ion
• Combined ion exchange is additive
Combined ion exchange (CIX)

Experimental design

- Cedar Key, Yankeetown, Palm Springs groundwater
  - DOC: 3–10 mg/L
  - Hardness: 300–440 mg/L as CaCO₃
- Anion exchange resin: MIEX-Cl
- Cation exchange resin: Amberlite 200C-Na
- Multiple-loading jar tests
  - Bed volumes (BVs)
  - 1000 BVs MIEX-Cl
  - 250 BVs A200C-Na
- NaCl regeneration (2%, 20%)
CIX treatment of groundwater

- 67–85% DOC removal, 1000 BV anion exchange (composite)
- ~50% hardness removal, 250 BV cation exchange (composite)

CIX treatment of NF concentrate

Experimental design

- NF concentrate from 2 membrane plants in FL
  - DOC: 33, 56 mg/L
  - Hardness: 960, 1000 mg/L as CaCO$_3$
  - Sulfate: 830, 71 mg/L
- Anion exchange resin: MIEX-Cl
- Cation exchange resin: Amberlite 200C-Na
- Multiple-loading jar tests
  - 200 BVs MIEX-Cl
  - 83 BVs A200C-Na
- NaCl regeneration (30%)
CIX treatment of NF concentrate

- 70–80% DOC removal, 50% sulfate removal, 90% hardness removal


- CIX produced similar water composition as NF feed water
Conclusions

• CIX treatment of groundwater achieved >70% DOC removal (MIEX-Cl resin) and >50% hardness removal (A200C-Na resin) in composite samples corresponding to 1000 BVs of anion exchange and 250 BVs of cation exchange depending on 2% or 20% NaCl regeneration solution.
• CIX removed DOC, sulfate, and hardness from NF concentrate to produce treated concentrate with similar characteristics as NF feed water.
Combined ion exchange (CIX) pilot plant
CIX pilot plant

Experimental design

• Cedar Key
  • DOC: ~5 mg/L
  • Hardness: ~300 mg/L as CaCO₃
• Anion exchange resin (AER): A-72 Thermax
• Cation exchange resin (CER): T-42 Thermax
• Pilot plant operation
  • Down flow columns
  • Resin ratio: 4 L AER-to-4 L CER
  • 0.5 gpm
• Regeneration: NaCl vs KCl regeneration (12% m/v)
CIX pilot plant, ongoing work

- Regeneration operation, e.g., precipitation
- Effectiveness of NaCl vs. KCl regeneration; disposal
- Lead–lag column operation
- Completely mixed CIX
- NaCl vs. NaHCO$_3$ regeneration (anion exchange only)
- Process modeling (w/ USF, WINSSS)
- Life cycle assessment (w/ USF, WINSSS)
- Decision support tool (w/ USF, WINSSS)
CIX pilot plant, ongoing work

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Thank you

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Other resource on Ion Exchange and CIX