Effect of ferroferric oxide on batch anaerobic treatment of high strengthen synthetic wastewater

Qidong Yin
Graduate School at Shenzhen
Tsinghua University
Sep 16, 2016
Contents

• Background
• Materials and Methods
• Results and Discussions
• Conclusions
1 Background
1.1 Anaerobic treatment

- Anaerobic treatment is a sustainable technology

- A severe environmental issue

- Water Reuse
- Energy Recovery

- Methane Production
- Sustainable Technology
1.1 Anaerobic treatment

- **Three-step mechanisms**

1. **Complex organic matters**
   - Hydrolysis/Acidification

2. **Small organic matters**
   - Hydrogenesis/Acetogenesis

3. **Acetate/Formate/H₂**
   - Methanogenesis

   **CH₄, CO₂**

- **Syntrophic Communities**: The complete conversion from organic matters to methane requires a microbial consortium composed of various types of species.
1.2 Interspecies electron transfer, IET

- **Interspecies electron transfer (IET)**

  - **Interspecies H₂ transfer**
    - *Methanothermus, Methanocaldococcus*

  - **Interspecies formate transfer**
    - *Methanobacterium, Methanothermococcus*

  - **Direct interspecies electron transfer**
    - *Methanosaeta, Methanothermobacte, Methanosarcina*

  - **Electron Transfer (H₂/Formate)**

  - **Production**
    - **Acidogenic bacteria**

  - **Reduction**
    - **Methanogens**

  - **CH₄, CO₂**
    - **Production**

  - **Syntroph**
1.3 Direct interspecies electron transfer, DIET

- DIET is a new mechanism

DIET means acidogenic bacteria (*Geobacter*) can transfer electron to methanogens directly using its conductive pili or outer membrane cytochromes, rather than H$_2$/Formate.

(Rotaru et al. 2013. A new model for electron flow during anaerobic digestion: direct interspecies electron transfer to Methanosaeta for the reduction of carbon dioxide to methane.)
1.3 Direct interspecies electron transfer, DIET

- Conductive materials

- Dosing conductive materials could accelerate the electron transfer among syntrophic communities.

![Diagram showing electron transfer between Acidogenic bacteria, Pili/Cytochromes, Conductive materials, and Methanogens, with CH₄, CO₂ as a product.](image-url)
1.3 Direct interspecies electron transfer, DIET

- Conductive materials

  Conductive materials can facilitate the methanogenesis.

<table>
<thead>
<tr>
<th>Conductive materials</th>
<th>Carbon source</th>
<th>Effect</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon materials</td>
<td>Glucose/ Ethanol</td>
<td>Facilitate CH$_4$ production rate/Shorten lag phase</td>
<td>Rotaru et al., 2014; Liu et al., 2012; Chen et al., 2014; Luo et al., 2015</td>
</tr>
<tr>
<td>(GAC/ carbon cloth/ biochar)</td>
<td></td>
<td>Facilitate the consumption of VFA</td>
<td></td>
</tr>
<tr>
<td>Magnetite (Fe$_3$O$_4$) / Hematite (Fe$_2$O$_3$)</td>
<td>Acetic acid/ Propionic acid/ Butyric acid/ Beef extract</td>
<td></td>
<td>Kato et al., 2012; Carolina et al., 2014; Yamada et al., 2015; Li et al., 2015; Zhu et al., 2015</td>
</tr>
</tbody>
</table>
1.3 Direct interspecies electron transfer, DIET

- Conductive materials
  - Conductive materials facilitated the production rate and shortened the lag phase during CH$_4$ production.

![Graph](Li et al. 2015)

![Graph](Luo et al. 2015)
1.4 Research Purposes

The aims of this study were to

- Examine the effect of conductive material $\text{Fe}_3\text{O}_4$ on the performance of anaerobic treatment of high strengthen synthetic wastewater.

- Compare the effect of $\text{Fe}_3\text{O}_4$ on anaerobic sludge acclimated with different carbon substrates.
2 Materials and Methods
2 Materials and Methods

- **System operation**
  - 2 ASBR: Starch based reactor/ Tryptone based reactor
  - COD concentration: 3 g COD/L (starch or tryptone)
  - Starch and tryptone were used to represent carbohydrate and protein substrate, respectively.

**Operating conditions**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>ASBR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume</td>
<td>2 L</td>
</tr>
<tr>
<td>HRT</td>
<td>48 h</td>
</tr>
<tr>
<td>SRT</td>
<td>33 d</td>
</tr>
<tr>
<td>Temperature</td>
<td>35°C</td>
</tr>
<tr>
<td>Operation mode</td>
<td>23 h anaerobic (5min filling) +1 h settling (5min decanting)</td>
</tr>
</tbody>
</table>
2 Materials and Methods

- **Batch effect by the dosage of Fe$_3$O$_4$**

  ![Diagram](https://via.placeholder.com/150)

- **Experimental conditions**
  - Conductive material
  - Groups: Control group/ Fe$_3$O$_4$ group
  - Inoculated Sludge: taken from ASBRs

### Operating condition

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume</td>
<td>500 mL</td>
</tr>
<tr>
<td>Mixer speed</td>
<td>170 rpm</td>
</tr>
<tr>
<td>Temperature</td>
<td>35°C</td>
</tr>
</tbody>
</table>
3 Results and Discussions
3.1 Batch experiments

- **Short term effect by the dosage of Fe$_3$O$_4$**

The $R_{\text{max}}$ was increased by 35.3% and the lag time was shortened by 48% after dosing Fe$_3$O$_4$.

Acetic acid consumption rate was also improved.

<table>
<thead>
<tr>
<th>Reactor</th>
<th>Ultimate CH$_4$ yield (mL)</th>
<th>Lag phase $\lambda$ (h)</th>
<th>Maximum production rate (mL/h)</th>
<th>Correlation coefficient $R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>117.3</td>
<td>5.0</td>
<td>5.1</td>
<td>0.999</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>112.5</td>
<td>2.6</td>
<td>6.9</td>
<td>0.995</td>
</tr>
</tbody>
</table>
3.1 Batch experiments

- **Short term effect by the dosage of Fe₃O₄**
  
  The addition of Fe₃O₄ had little effect on the CH₄ production rate or the lag phase.
  
  The produced acetic acid concentration was increased.

<table>
<thead>
<tr>
<th>Reactor</th>
<th>Ultimate CH₄ yield (mL)</th>
<th>Lag phase λ (h)</th>
<th>Maximum production rate (mL/h)</th>
<th>Correlation coefficient R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>73.5</td>
<td>5.4</td>
<td>2.8</td>
<td>0.999</td>
</tr>
<tr>
<td>Fe₃O₄</td>
<td>80</td>
<td>6.4</td>
<td>3.3</td>
<td>0.999</td>
</tr>
</tbody>
</table>
3.1 Batch experiments

- Short term effect by the dosage of different \( \text{Fe}_3\text{O}_4 \) concentrations

![Graph](a) 

- Generally, the \( R_{\max} \) was increased and the lag phase became shorter with the \( \text{Fe}_3\text{O}_4 \) concentration.
- Acetic acid consumption rate was faster.

<table>
<thead>
<tr>
<th>Reactor</th>
<th>Ultimate ( \text{CH}_4 ) yield (mL)</th>
<th>Lag phase ( \lambda ) (h)</th>
<th>Maximum production rate (mL/h)</th>
<th>Correlation coefficient ( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>77.35</td>
<td>9.19</td>
<td>4.31</td>
<td>0.9931</td>
</tr>
<tr>
<td>F2.5</td>
<td>72.67</td>
<td>7.51</td>
<td>4.98</td>
<td>0.9931</td>
</tr>
<tr>
<td>F5</td>
<td>66.56</td>
<td>6.96</td>
<td>5.19</td>
<td>0.9967</td>
</tr>
<tr>
<td>F10</td>
<td>68/96</td>
<td>6.56</td>
<td>5.51</td>
<td>0.9981</td>
</tr>
<tr>
<td>F15</td>
<td>65.38</td>
<td>5.51</td>
<td>5.54</td>
<td>0.9980</td>
</tr>
<tr>
<td>F20</td>
<td>58.06</td>
<td>4.31</td>
<td>4.85</td>
<td>0.9963</td>
</tr>
</tbody>
</table>
3.1 Batch experiments

- Short term effect by the dosage of different Fe\textsubscript{3}O\textsubscript{4} concentrations

- Different Fe\textsubscript{3}O\textsubscript{4} concentrations all led to longer lag phase.
- Only the R\textsubscript{max} of F2.5 and F5 increased.
- No significant improvement was found.

<table>
<thead>
<tr>
<th>Reactor</th>
<th>Ultimate CH\textsubscript{4} yield (mL)</th>
<th>Lag phase λ (h)</th>
<th>Maximum production rate (mL/h)</th>
<th>Correlation coefficient R\textsuperscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>45.37</td>
<td>4.28</td>
<td>3.04</td>
<td>0.9931</td>
</tr>
<tr>
<td>F2.5</td>
<td>47.82</td>
<td>4.93</td>
<td>3.40</td>
<td>0.9931</td>
</tr>
<tr>
<td>F5</td>
<td>52.57</td>
<td>4.92</td>
<td>3.48</td>
<td>0.9967</td>
</tr>
<tr>
<td>F10</td>
<td>44.71</td>
<td>6.37</td>
<td>2.98</td>
<td>0.9981</td>
</tr>
<tr>
<td>F15</td>
<td>56.71</td>
<td>4.8</td>
<td>2.46</td>
<td>0.9980</td>
</tr>
<tr>
<td>F20</td>
<td>54.39</td>
<td>5.0</td>
<td>1.79</td>
<td>0.9963</td>
</tr>
</tbody>
</table>
3.1 Batch experiments

- Short term effect of Fe$_3$O$_4$ (10g/L) on hydrolysis and acidification phase of tryptone

![Graph showing VFAs production over time for control and Fe$_3$O$_4$ groups.]

- BES was added to inhibit the activity of methanogens (BES: 2-bromoethanesulfonic acid sodium salt)

- The control group and the Fe$_3$O$_4$ group had similar trend of VFAs production, indicating that short term dosage of Fe$_3$O$_4$ might not facilitate the hydrolysis and acidification of tryptone.

- Similar results were obtained by the metabolic end product of hydrolysis and acidification, acetic acid.
3.1 Batch experiments

- **Short term effect of Fe₃O₄ on methanation**

- Only acetate was added as carbon substrate, instead of tryptone.
- Without hydrolysis and acidification, adding Fe₃O₄ seemed to hinder the activities of methanogen.
- The $R_{\text{max}}$ was decreased by 73.1% and the lag time was delayed by 9.7%.

<table>
<thead>
<tr>
<th>Reactor</th>
<th>Ultimate CH₄ yield (mL)</th>
<th>Lag phase $\lambda$ (h)</th>
<th>Maximum production rate (mL/h)</th>
<th>Correlation coefficient $R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>72.6</td>
<td>17.91</td>
<td>6.42</td>
<td>0.9915</td>
</tr>
<tr>
<td>Fe₃O₄</td>
<td>67.87</td>
<td>19.64</td>
<td>1.72</td>
<td>0.9828</td>
</tr>
</tbody>
</table>
3.2 Microbial community

- **Short-term effect – Microbial community**

- **Methanosarcina** (66.28%) was the dominant methanogen in the sludge acclimated with tryptone and *Methanosarcina* was proved to accept electrons via DIET.

- **Methanobacterium** (92.80%) was predominant in the sludge acclimated with starch. And its ability of DIET is still controversial.
4 Conclusions
Fe$_3$O$_4$ accelerated methane production for microorganisms acclimated with protein-based substrate.

Acceleration only occurred when the interspecies electron transfer between acidogenic bacteria and methanogen existed.

Organic carbon affected the acclimated microbial communities, leading to different performance when dosing conductive materials.
Thank you!