Alleviating sulfide toxicity using biochar during anaerobic treatment of high-sulfate wastewater with sulfur recovery


*Department of Molecular Biosciences and Bioengineering, University of Hawai`i at Manoa, Honolulu, HI 96822, USA, mjcha3@hawaii.edu, surendra@hawaii.edu, khanal@hawaii.edu
**Plant and Soil Sciences, University of Delaware, Newark, DE 19716, USA, jaisi@udel.edu
***School of Environmental Science and Engineering, Sun Yat-sen University, Guangzhou, PR China, lvhui3@mail.sysu.edu.cn

Abstract: This study examined use of biochar to alleviate sulfide toxicity during anaerobic treatment of high-sulfate wastewater with concomitant recovery of sulfur. At the highest sulfate concentration tested (6,000 mg SO4²⁻/L), the unionized dissolved sulfide (DS) of 55 mg S/L resulted in built-up of total volatile fatty acids concentration up to 2,500 mg/L as acetic acid (HAc), and the reactors were on the verge of failure. After recirculation of biogas through biochar, > 98% of gaseous H2S was removed, DS reduced to < 8 mg S/L, and the reactors recovered to stable state. 16S rRNA gene sequencing analyses revealed an increase in relative abundance (RA) of sulfate reducers (Desulfovibrio) and a decrease in RA of methanogens (Methanobacterium, Methanoseta and Methanomassilicocaceae) at increasing sulfate concentrations. However, after integration of biochar column, RA of Desulfovibrio dropped significantly with increase in RA of Methanobacterium group. This study provided a new avenue for use of biochar for alleviating sulfide toxicity, cleaning biogas and recovering sulfur as macro-nutrient for land application in sulfur deficient soils.

Keywords: Sulfate-laden wastewater; anaerobic treatment; sulfur-rich biochar

Session: Resource recovery

Introduction

Anaerobic process is widely adopted for treating high-strength wastewaters with concomitant recovery of bioenergy (Khanal, 2008). However, anaerobic treatment of sulfate-laden wastewater generates hydrogen sulfide (H2S) due to dissimilatory sulfate reduction. H2S is highly corrosive and deters the quality of biogas as an energy resource. Importantly, it imposes toxicity to anaerobes, especially methanogens in aqueous phase, which could lead to process failure (Khanal and Huang, 2003). Current methods of sulfide removal such as use of chemicals (various metal ions and alkali chemicals) is costly and often generate chemical wastes, and biological method is slow and less effective, especially at high sulfide concentration (Khanal and Li, 2016). Above all, both methods do not recover sulfur. Here we employed biochar, a carbonaceous byproduct obtained during the pyrolysis of biomass, as an efficient and cost-effective removal of H2S by recirculating the sulfide-laden biogas through an external biochar column with potential for reuse of sulfur-rich biochar as macro-nutrient in sulfur deficient soils (David et al., 2016; Kanjanarong et al., 2016). Few studies reported H2S removal using biochar (Shang et al., 2016; Kanjanarong et al., 2016). However, in depth studies elucidating the mechanisms of H2S removal by biochars produced at different conditions and sources, and the subsequent effect on microbial communities in anaerobic process due to alleviation of sulfide toxicity are limited. This study highlights the effects of H2S removal by biochar on anaerobic process performance and process microbiology, especially the diversity and relative abundance (RA) of methanogens and sulfate reducers. Additionally, we also examined H2S removal mechanism.

Material and Methods

Four (R1, R2, R3 and R4), 5 L working volume continuous-stirred tank reactors (CSTR) as described in Figure 1.1 were operated simultaneously at mesophilic condition (35 ± 2 °C). The organic loading rate (OLR) was gradually increased from 1 to 5 g chemical oxygen demand
(COD)/L-day while maintaining the same hydraulic retention time (HRT) of 10 days. The biogas produced was recirculated through the bottom of the reactor to achieve mixing. Reactors performance were evaluated based on their resilience to high sulfate concentration. Once steady state was achieved at OLR of 5 g COD/L-day, potassium sulfate was supplemented in feed as a sulfate source at increasing levels (4,000, 5,000 and 6,000 mg SO$_4^{2-}$/L) until reactors showed signs of perturbations due to sulfide toxicity. At this point, the biogas was passed through an external biochar column before recirculating back to the reactors. The biochars used in column, softwood- and hardwood-biochar produced at 550 and 800 °C (labeled as BS550, BS800, BH550 and BH800, respectively), were analyzed for composition (elemental and proximate) and surface texture.

Furthermore, breakthrough test was conducted to evaluate their adsorption capacities. All the analyses were conducted in triplicates and statistical analysis was carried out using JMP Pro statistical software (v.12, SAS Institute Inc., USA). For microbial community analysis, 16S rRNA genes of bacteria and archaea were amplified by 338F/806R/515F and 907R primer sets, respectively, and sequenced on an IlluminaHiseq2500 platform.

## Results and Conclusions

The performance of reactors R1, R2, R3 and R4 did not vary significantly during initial OLRs. Moreover, there was no significant difference in the treatment efficiency between multi- and single-fed systems (p>0.2), which could be due to the limited height of the reactors. However, at higher loading conditions (OLR of 4 g COD/L-day) and absence of support media, the performance of reactor R4 started to deteriorate before reaching the OLR of 5 g COD/L-day and it was discontinued (Figure 1.2). At OLR of 5 g COD/L-day and sulfate concentration of 6,000 mg SO$_4^{2-}$/L, all three reactors (R1, R2 and R3) started to show the sign of sulfide toxicity with corresponding free dissolved sulfide (DS) of 55 mg/L and biogas H$_2$S level of 65,000 ppm (Figure 1.3F) as apparent from decreasing methane yield (Figure 1.3C), and increasing volatile fatty acids (VFAs) (Figure 1.3A) and total organic carbon (TOC) (Figure 1.3B) concentrations in effluent.

Once the biogas recirculation through biochar column was initiated, H$_2$S in biogas and free DS dropped to 100 ppm and 8 mg S/L, respectively, with concomitant improvement in reactor performance. van Krevelen diagram (Figure 1.4) illustrates the thermal modification mechanism during biochar production that has significant effect on biochar sorption properties. Pyrolysis at higher temperature (800 °C) results in loss of more surface functional groups as OH’ and C-bound O and H atoms than that of biochar produced at lower temperature (550 °C) thereby resulting in less polar sites available for sulfide oxidation to sulfate. The adsorption capacity of the biochars tested ranged from 228.1 mg/g to 262.6 mg/g (Table 1.1) with BS550 having the highest adsorption capacity followed by BH550, BH800 and BS800 which is in agreement with van Krevelen diagram. However, no significant difference in reactor performance was observed among biochars (p>0.2).

The RA of Desulfovibrio increased with increasing sulfate concentration from 4,000 to 6,000 mg SO$_4^{2-}$/L with an apparent inhibition of methanogens (Methanobacterium, and Methanoseta) as evident from their decreasing RA (Figure 1.5). The dominant group among the methanogens was the hydrogenotrophic methanogens, Methanobacterium (75%). In general, the aceticlastic methanogens (Methanosarcina and Methanosaeta) are much more sensitive to sulfide than the hydrogenotrophic methanogens (Methanobacterium) (Zabranska and Pokorna, 2017). The biochar removed >98% of gaseous H$_2$S and 85% DS, thereby alleviating sulfide toxicity to methanogens and promoting the stability of the anaerobic process. Additionally, the sulfur-rich biochar could provide a new opportunity as a source of macro-nutrient in sulfur deficient soils.

Figure 1.2 Reactor performance at different OLRs. (A) VFAs. (B) TOC. (C) Methane yield.
Figure 1.3 Reactor performance with and without biochar. (A) VFAs. (B) TOC. (C) Methane yield. (D) Free sulfide. (E) Dissolved sulfide. (F) H₂S concentration.

Figure 1.4 van Krevelen diagram showing changes in O/C and H/C ratios from feedstocks to biochars during pyrolysis.

Table 1.1 Adsorption capacity, H₂S breakthrough time, and saturation time for the BS550, BS800, BH550, and BH800 samples.

<table>
<thead>
<tr>
<th></th>
<th>Adsorption capacity (mg H₂S /g)</th>
<th>Breakthrough time (sec)</th>
<th>Saturation time (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BS550</td>
<td>262.6</td>
<td>10</td>
<td>60</td>
</tr>
<tr>
<td>BS800</td>
<td>228.1</td>
<td>7</td>
<td>70</td>
</tr>
<tr>
<td>BH550</td>
<td>239.1</td>
<td>10</td>
<td>60</td>
</tr>
<tr>
<td>BH800</td>
<td>229.5</td>
<td>5</td>
<td>30</td>
</tr>
</tbody>
</table>

Figure 1.5 Relative abundance (%) of MPA and SRB within the reactors R1 (A), R2 (B) and R3 (C) during anaerobic treatment of wastewater with increasing concentration of sulfate (4,000, 5,000 and 6,000 mg SO₄²⁻/L) without biochar and at 6,000 mg SO₄²⁻/L with biochar treatment.
References