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Synthetic effect between iron oxide and sulfate mineral on the anaerobic transformation of organic substance

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HIGHLIGHTS

- Hematite and gypsum in the mixture promote anaerobic degradation of substrate.
- Hematite and gypsum in the mixture reduce the GHG releasing.
- Addition of hematite increases the anaerobic digestion process.
- Iron oxide precipitates and eliminate the negative impact of S^{2-}.
- Ca^{2+} released from gypsum generates calcite.

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ABSTRACT

Synthetic effect between sulfate minerals (gypsum) and iron oxide (hematite) on the anaerobic transformation of organic substance was investigated in the current study. The results showed that gypsum was completely decomposed while hematite was partially reduced. The mineral phase analysis results showed that FeS and $CaCO_3$ was the major mineralization product. Methane generation process was inhibited and inorganic carbon contents in the precipitates were enhanced compared to the control without hematite and gypsum. The inorganic carbon content increased with the increasing of hematite dosages. Co-addition of sulfate minerals and iron oxide would have a potential application prospect in the carbon sequestration area and reduction of the greenhouse gas release. The results would also reveal the role of inorganic mineral in the global carbon cycle.

1. Introduction

Under anaerobic condition microbial methanogenic process was a pathway for carbon transformation. Methane is one of the main greenhouse gases and the greenhouse effect of CH_4 is 23 times than that of CO_2 (Houghton et al., 2001). Nevertheless, there are a number of sources in nature that could release methane such as wetlands, river, lake sediments, landfills, intensive animal farms, etc. Most of these sites are rich of organic matters and would release large quantities of methane into the atmosphere (Rodionow et al., 2006). How to suppress methane production using low cost and feasible method is an important scientific issue need to explore urgently. Adding chemical inhibitors for methane-producing bacteria (MPB) was one of the most popular methods (Liu et al., 2011). For example, chlorinated methane, the trichloro acetylene, bromochloromethane, chlorinated fatty acids and many other halogen compounds had been used to effectively inhibit methane production because of their toxic effects on methanogen (Russell and Martin, 1984; Mass et al., 2000). However, use of these methane-inhibitors has certain ecological risk for secondary pollution since they mostly belong to environmental pollutants.

Sulfate-reducing bacteria (SRB) process had been extensively used in the treatment of acid mine drainage and bioremediation of organic pollutants contaminated sites (Bai et al., 2013; Chang et al., 2003; Zhou et al., 2013). Over the past years, competition of SRB with MPB and its environmental effects has been investigated significantly (Chou et al., 2008; Jakobsen and Postma, 1999). According to a thermodynamic ladder of electron accepting processes, the anaerobic microbiological order was SRB > MPB (Bethke et al., 2011). Compared with the above

Abbreviations: MPB, methane-producing bacteria; SEM, scanning electron microscopy; SRB, sulfate-reducing bacteria; TIC, total inorganic carbon; TOC, total organic carbon; XRD, X-ray diffraction method.

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inhibitors, abundant materials of sulfate minerals in nature could be potential electron acceptor materials for the inhibition of MPB (Yao et al., 1999). This had been developed to depress methane production and promote organic carbon fixation (Varjo et al., 2003).

SRB accelerates the decomposition of organic pollutants, while the metabolite product of H_2S would have chemical toxicity to the microorganism. For example, it was found 547 mg/L of hydrogen sulfide could completely inhibit the growth of SRB (Reis et al., 1992). Iron oxide has been applied extensively in the clarification process of biogas from the anaerobic digesters (Cantrell et al., 2003). However, it was lack of awareness of how iron oxide and sulfate minerals together impact the anaerobic conversion of organic matter. Therefore, the purpose of this paper is to explore the impact of iron oxide and sulfate minerals on the anaerobic decomposition and conversion of beef extract peptone. This would help to understand more about the regulation mechanisms of organic carbon conversion.

2. Methods

2.1. Inoculums

Anaerobic sludge from Wangxiaoying sewage treatment plant was used to obtain enriched SRB inoculums. Enriched MPB inoculums were achieved using the anaerobic granular sludge in Fengyuan chemical plant. Gypsum was collected the mineral plant in DingYuan, Anhui province. Gypsum was ground and dilute acid was added to remove the carbonate. Artistically synthetic hematite (Fe_2O_3) was used as the representative of iron oxides. Beef extract peptone medium was used as substrate (Roden and Urrutia, 1999).

2.2. Experimental design

150 mL serum bottles were used and the inoculated MPB and SRB solution was 5 mL, respectively. Six groups were designed and named as Y1, Y2, Y3, Y4, Y5 and Y6. For Y1 no minerals were added. For Y2-Y5 the added gypsum was fixed at 5 g, while the mass of hematite were 5, 2.5, 0.5 and 0 g. For Y6 only 5 g hematite was added. After minerals, nutrients and enriched anaerobic microorganisms were added, the serum bottles were purged with nitrogen gas to drive out oxygen, sealed and placed in incubator with the temperature of 35 ± 1 °C. Each group has four replicates. Two duplicate were used for measuring gaseous products and gas composition while the other two used for testing liquid samples which were used to measure pH, SO_4^{2-}/S^{2-}, total organic carbon (TOC), total inorganic carbon (TIC), Fe^{3+}/Fe^{2+}. Solid samples were taken from the serum bottles and vacuum-dried for the determination of inorganic and organic carbon at the end of reaction.

2.3. Analytical methods

CH_4 was analyzed on Japan Shimadzu GC-2010 with a packed column (RTX-wax, 30 m × 0.25 mm × 0.25 μm). TOC, TIC and CO_2 were determined on Germany Jena C/N 2100 TOC analyzer. SO_4^{2-} and Fe^{2+} were measured using barium chromate and *o*-phenanthroline spectrophotometric method, respectively. H_2S and S^{2-} were analyzed using gas phase molecular absorption spectrometry (Shanghai angelides AJ-2100 type). Mineralogical changes were characterized by scanning electron microscopy (SEM) and X-ray diffraction method (XRD).

3. Results and discussion

3.1. Production of gaseous component

Compared to control (Y1), the methane that was produced in Group Y5 with gypsum addition was reduced significantly by approximately 40.2% (Fig. 1a). In Group Y6 with hematite addition, the methane production rate was increased significantly and methane yield was increased by 5%. In Groups Y2, Y3 and Y4 with gypsum in addition of hematite, methane production rate was much faster than that of the control (Group Y1), but eventually the yield of methane was reduced by 9–15%.

Fig. 1b showed that at the early stage the release of CO_2 (Group Y1) was relatively close to that in Group Y5, but the production was lower than that in other groups. And the final CO_2 releasing volume in control group was higher than that in other groups with minerals addition. The variation in CO_2 and CH_4 production potentials in Groups 2–4 were pretty similar, which indicated that the addition of hematite improved the generation rate of both methane and CO_2 in the early stage of the reaction (Fig. 1).

The total production of H_2S in each group was Y5 > Y4 > Y3 > Y2 > Y1 > Y6 (Fig. 1c). When gypsum and hematite coexisted, the sulfide would be precipitated as FeS. The elemental sulfur in Groups Y1 and Y6 might come from the beef extract and peptone in the culture. The relative higher concentration of H_2S in Groups 4 and 5 was attributed to the lower iron ion or iron oxide in the culture.

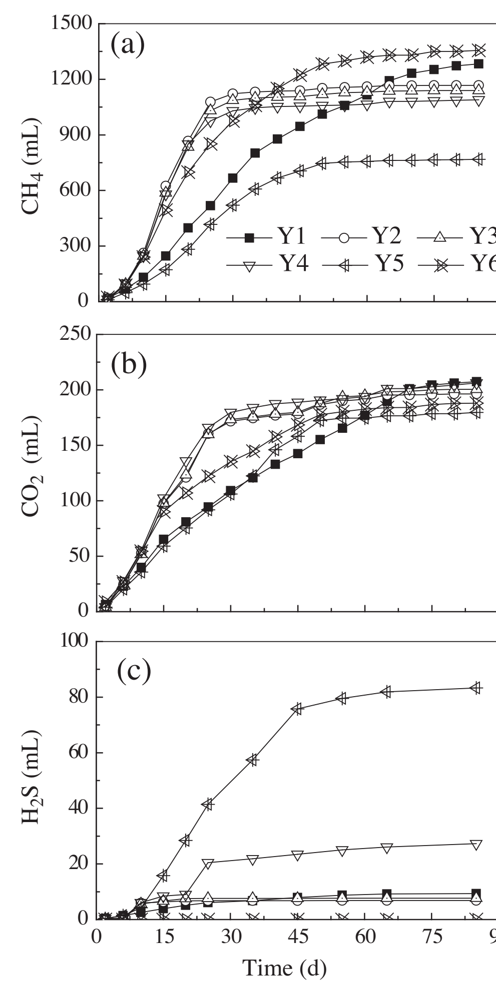

Fig. 1. Accumulated gas production of (a) CH_4, (b) CO_2 and (c) H_2S.