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学位論文題 Application of Micro-Nano Bubbles on Bioconversion of Carbon Dioxide and Hydrogen to Methane

(マイクロナノバブルを用いた H_2 と CO_2 からメタンへの生物的変換)

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論　文　の　要　旨
Abstract of thesis

Bioconversion of CO_2 and H_2 into CH_4 by hydrogenotrophic methanogens can simultaneously realize CO_2 removal and renewable biofuel production. However, the low gas-liquid mass transfer (k_La) of H_2 limits the commercial application of this bioconversion. The micro-nano bubbles (MNBs) had been applied in many fields including medical, wastewater purification, food processing, marine and agriculture applications, due to the high specific area and high stagnation in liquid phase. The existence of MNBs has been proved to enhance the growth of plants and animals. Up to now, however, little information can be found on the combination of MNBs with anaerobic microorganisms.

Consequently, this study applied the MNBs to the anaerobic procedure, bioconversion of CO_2 to CH_4. Firstly, the feasibility of MNBs for enhancement of bioconversion efficiency was investigated. On the basis of detecting the methane production, VFAs variation, biomass enrichment, carbon and hydrogen balance were analyzed to evaluate the effect of MNBs on the bioconversion. Energy consumption was monitored to assess the potential of MNBs for practical applications. Secondly, in order to reveal the mechanism of the effect induced by the nano scale bubbles, except the methane and VFAs productions, the unique coenzyme of methanogens (coenzyme F_{420}) was also measured. Considering the trace metals was the main components of coenzymes, the intracellular concentrations and different fractions of trace metals were analyzed. The effect of nano bubbles (NBs) on the physicochemical properties of pure medium was also analyzed by detecting the zeta potential and particle distributions. Finally, the experiment was carried out by pre-loading the air NBs to the bioreactors under varied Fe and cysteine concentrations, aiming to explore the effect of NBs in different conditions. In this part, the soluble sulfide concentration was measured to identify the effect was caused by the micro-oxygen condition or the nano bubbles.

The dissertation is divided into 5 chapters. In the chapter 1, the author first gave a brief introduction related to the

bioconversion procedure. After stating the limitations， the various solutions were summarized. Then the characteristics and related applications of MNBs were demonstrated. Finally, the author proposed research objectives at the end of this chapter. In chapter 2, the author tested and compared two stirred tank reactors (STRs) equipped with a micro-nano sparger (MNS) and common micro sparger (CMS), respectively. MNS was found to display superiority to CMS in methane production with the maximum methane evolution rate (MER) of 171.40 mmol/L_R/d and 136.10 mmol/L_R/d, along with a specific biomass growth rate of 0.15 /d and 0.09 /d, respectively. Energy analysis indicated that the energy-productivity ratio for MNS was higher than that for CMS.

In chapter 3, the effect of NBs on the hydrogenotrophic methanogens was investigated by preparing liquid medium with or without H_2/CO_2 mixture nano bubbles. The results showed that both methane production and VFAs degradation were enhanced by the pre-supplementation of NBs in the liquid. The higher coenzyme F_{420} content was obtained in nano-bubble (NB) group with content of 1.84 μmol/g-VS, while 1.56 μmol/g-VS for control group. The intracellular Fe contents in NB group were higher than the control group, with the concentration of 1159.53±20.34, 1035.28±12.01 μg/g-VS, respectively. For the metal speciation, the higher percentage of acid soluble and exchangeable fraction, while lower percentage of organic matter and sulfide fractions in the NB group were achieved than the control group. The NBs may enhanced the mass transfer and bioavailability of trace metals.

In chapter 4, the effect of air NBs on bioconversion of H_2 and CO_2 to CH_4 was investigated under different initial iron and cysteine concentrations. Results showed that for the inoculated groups, the stimulation for methane production by air NBs was more obvious under lower iron (50 μM) or cysteine concentrations (3 mM). The methane production was inhibited at 100 μM Fe concentration, while the more obvious inhibition was obtained in NB group. The soluble sulfide concentration increased for all the NB groups compared with the groups without bubbles, especially under 6 mM cysteine concentration (0.62 mg/L in NB group, 0.42 mg/L in control group). For the pure medium, the bubbles may combine with the particles, which was proved by an increased zeta potential (from -31.80±1.90 to -26.62±2.05). While the oxidation-reduction potential (ORP) before and after introduction of NBs did not change obviously. For the metal speciation analysis, the increase in Fe concentrations led to an increase in adsorbed fractions, and the existence of NBs enhanced this increment.

In chapter 5, the author summarized the overall conclusions and future research perspectives.

審 査 の 要 旨
Abstract of assessment result

This research provided a successful application of MNBs for the anaerobic bioconversion of CO_2 to CH_4. The existence of MNBs can simultaneously realize high gas-liquid mass transfer, and high biomass enrichment, with a low energy consumption. The micro scale bubbles enhance the bioconversion efficiency by improving the specific surface area. While, both the coenzyme content and intracellular metal content was increased after introducing the nano scale bubbles. The NBs also had a positive effect on the bioavailability of trace metals. The increased particle size and zeta potential of the pure medium after inducing the NBs indicated the combination of bubbles and particles. The higher mass transfer of trace metals in the NB group may result from more chance for the methanogen cells to contact with the trace metals. The effect and mechanism exploration of MNBs in this study is promising for applying the MNBs in practice in the anaerobic process or the microbial field.

The final examination committee conducted a meeting as a final examination on 20th July, 2018. The applicant provided an overview of dissertation, addressed questions and comments raised during Q&A session. All of the committee members reached an agreement that the applicant has passed the final examination.

Therefore, the final examination committee approved that the applicant is qualified to be awarded the degree of Doctor of Philosophy in Environmental Studies.