Bioconversion of CO_2 to CH_4 and biogas upgrading using anaerobic granular sludge and Zero Valent Iron.

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Keywords: CO_2 utilization, methane, biogas upgrading, zero valent iron.
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Introduction

Carbon dioxide (CO_2) can be consider as one of the main reasons of climate change and global warming. The intense fossil fuel consumption due to industrial processes and energy production activities, considered to be the major cause of CO_2 elevated atmospheric levels (Daglioglu et al., 2019). Thus, any exploitation of CO_2 into various chemicals and other fuels not only will be an attractive solution to global warming but also will lead to fossil fuels replacement (Yang et al., 2017).

Up to date, most of the technologies that are mainly proposed for CO_2 mitigation, are physicochemical methods such as physical absorption using water scrubbing systems, physical absorption using organic solvents, chemical absorption using amine solutions, pressure swing adsorption (PSA) etc that involve high value materials or even intense conditions such as high temperature, pressure etc., (Saeidi et al., 2014).

The same technologies that mention above, are also used for biogas upgrading to biomethane. Biogas synthesis is mainly methane (40-60%) and carbon dioxide (60-40%) (Aryal et al., 2018) and achieving biogas upgrading to biomethane (> 95% CH_4) is essential primarily because it increases its calorific value and hence it can be easily stored or transported (Muñoz et al., 2015), (Angelidaki et al., 2018).

Several recent studies have examined an alternative process for CO_2 to CH_4 and biogas upgrading at mild conditions based on the utilization of CO_2 and H_2 by hydrogenotrophic methanogens according to Eq. (1).

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O \qquad \Delta G^0 = -130.7\ kJ/mol \quad (1)$$

In resent years, research in the addition of zero valent iron (ZVI) to anaerobic digestion process in order to enhance the biodegradation of waste and wastewater has become very popular. Particularly, ZVI contributed to higher chemical oxygen demand (COD) removal and methane production compared to no addition of ZVI (Hu et al., 2015). Up to date however, little research has been done on the use of ZVI and anaerobic granular sludge for the conversion of CO_2 as a sole carbon substrate to CH_4 and biogas upgrading.

ZVI under anaerobic aquatic condition (non-sulfidic, carbonate-buffered, pH~6) produced H_2 and oxidized according to Eq. (2) (Palacios et al., 2019).

$$Fe^{(0)} + HCO_3^- + H^+ \rightarrow FeCO_3 + H_2 \qquad \Delta G^0 = -79.9\ kJ/mol \quad (2)$$

Material and methods

Batch laboratory-scale anaerobic fermentation experiments were conducted using anaerobic granular sludge (3g of wet weight was added in 80 ml). For CO_2 conversion to CH_4, ZVI (fine powder) was added in various concentrations 25 g L^{-1}, 50 g L^{-1}, 75 g L^{-1} and 100 g L^{-1}. For biogas upgrading, ZVIS (zero valent iron scrap) was used in concentrations 100 g L^{-1}, 200 g $L^{-1}$and 300 g L^{-1}. The remaining volume (up to 80 ml) was filled with media (Angelidaki et al., 2009). Initial pH 6, CO_2 as a sole carbon source, triplicates serum bottles were done for each condition.For creating anaerobic conditions, CO_2 gas was introduced to each serum bottle for 10 min to remove oxygen, and then, the bottles were capped and sealed with butyl septa and aluminum crimps and stirred in a shaking incubator (100 rpm) at 33 °C. For biogas upgrading same procedure was followed using synthetic biogas (60% CH_4 – 40% CO_2). Gas composition (CH_4, CO_2, H_2, N_2, and O_2) was analyzed over time via a GC-TCD.

Results and discussion

The results for CO_2 utilization shown that the highest CH_4 production over time was found at 75 g L^{-1} of ZVI (69.2 % CH_4 in 18 days) followed by ZVI concentrations of 50 g L^{-1} and 100 g L^{-1} (around 53.8 % CH_4 in 18 days). For 25 g L^{-1} the concentration was considerably lower. The biogas upgrading shows that 200 g L^{-1} and 300 g L^{-1} of ZVSI in anaerobic granular sludge resulted in CH_4 composition of 95.5 % and 95.3%, respectively after 21 days. Interestingly, very little H_2 was detected in the headspace and this could be due to slow release of H_2 by ZVSI followed by immediate consumption by hydrogenotrophic methanogens.

Conclusions

This study tested a new approach for CO_2 conversion to CH_4 by using ZVI and anaerobic granular sludge under mild environmental conditions with CO_2 representing the sole carbon source. Importantly, due to the anaerobic

oxidation of ZVI, H_2 was produced and it was shown that hydrogenotrophic methanogens present in anaerobic granular sludge were the biocatalysts for the conversion of CO_2 to CH_4.
The optimum batch conditions for CO_2 conversion to CH_4 by anaerobic granular sludge were set at initial pH of 6 under daily pH regulation, with 75 g L^{-1} ZVI. Under these conditions, it was concluded that CO_2 is fully utilized from the headspace in 4 days and the maximum production of CH_4 is reached in around 6 days. The biogas upgrading to biomethane can be achieved in a batch system of anaerobic granular sludge and 200 g L^{-1} zero valent scrap iron in 21 days.

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