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

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Introduction

Carbon dioxide (CO_2) high levels in Earth's atmosphere, is strongly connected with global warming and climate changes. The intense fossil fuel consumption for industrial processes and energy production activities can be consider as the main contributor to this increase (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).

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).

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).

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

Up to date however, little research has been done on the use of ZVI or Zero Valent Scrap Iron (ZVSI) 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).

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

Results & Discussion

The results for CO_2 utilization using ZVI as a source of hydrogen by the anaerobic granular sludge at initial pH value 6, shown that the highest % of 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}, 100 g L^{-1}, 125 g L^{-1} (around 53 % CH_4 in 18 days) and 150 g L^{-1} (44,2 % CH_4 in 18 days) For the 25 g L^{-1} the concentration was considerably lower (21.8 % CH_4 in 18 days).

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. At the same time 100 g L^{-1} resulted in CH_4 composition of 90.7 % 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.

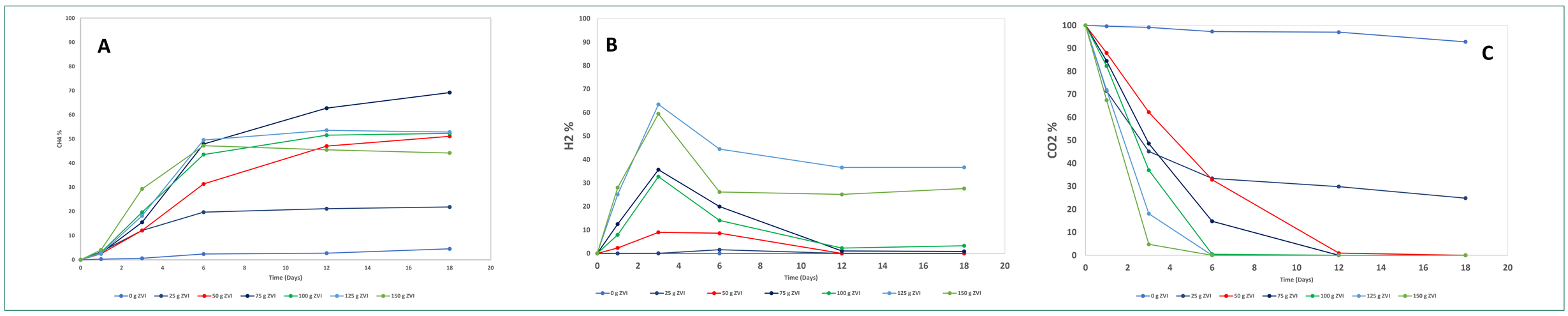

Figure 1: **A.** CH_4 production **B.** H_2 production and **C.** CO_2 utilization by anaerobic granular sludge under various ZVI concentrations (at initial pH 6)

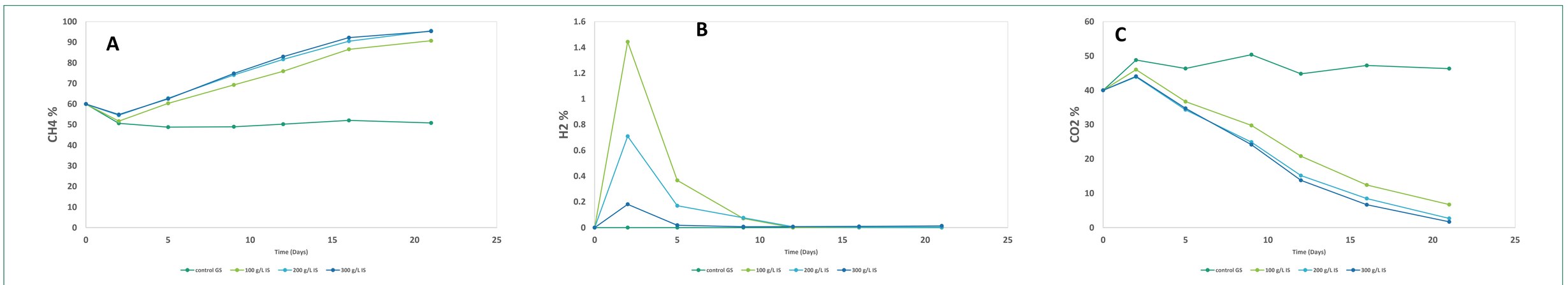

Figure 2: **A.** CH_4 production **B.** H_2 production and **C.** CO_2 utilization by anaerobic granular sludge (2g VS/L) under various ZVSI concentrations (at initial pH 6)

Conclusions

This study tested a new approach for CO_2 conversion to CH_4 by using ZVI and biogas upgrading with the addition of ZVSI, both using 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 act as biocatalysts for the conversion of CO_2 to CH_4. Especially for the biogas upgrading, the addition of ZVIS will contribute to increase biogas calorific value and have larger quantities of bio-methane that can be inserted into the grid of natural gas and utilized far away from the source of production.