

A Metal-Assisted Circular System for CO₂ Utilization and Methane Enhancement in Anaerobic Digestion.

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Introduction

Addressing climate change through biological CO₂ conversion is central to sustainable bioenergy strategies. This work aims to investigate a novel metal-assisted bioprocess for the conversion of CO₂ to CH₄, as well as biogas upgrading to biomethane, in an aquatic batch system using zero-valent iron (ZVI) and anaerobic granular sludge (AnGrSl) under mild environmental conditions. The biological reduction of CO₂ to value-added carbonic compounds such as methane offers a promising approach for mitigating its atmospheric accumulation and associated global warming. Compared to physicochemical CO₂ conversion methods, biological routes function under milder operational conditions, making them more energy-efficient and suitable for decentralized or off-grid applications (Vyrides et al. 2018).

Building on this foundation, the experimental results presented in this study show that the integration of sodium bicarbonate (NaHCO₃) into anaerobic systems consistently enhances CH₄ production. Bicarbonate serves both as a buffering agent and as a provider of soluble CO₂, which is more readily available for microbial uptake. When combined with ZVI, this synergistic system promotes rapid H₂ evolution and improved CH₄ yields (Andronikou et al. 2025).

From this dual function, a closed-loop process is proposed to further enhance sustainability. A NaOH solution can be used initially to absorb CO₂ and form NaHCO₃, which is then introduced into the bioreactor (Yoo et al. 2013). Within the system, the bicarbonate is utilized by methanogens while simultaneously accelerating ZVI activity. Once the soluble CO₂ is depleted, the same solution is extracted, re-flushed with CO₂, and recycled, establishing a circular approach to CO₂ capture and utilization (Constantinou et al. 2023).

This integrated system offers a cost-effective and low-energy strategy for biogas upgrading, supporting circular economy goals and aligning with climate mitigation targets. The potential of this process is demonstrated by the experimental outcomes in Figure 1, where elevated CH₄ content and effective CO₂ removal validate its technical feasibility.

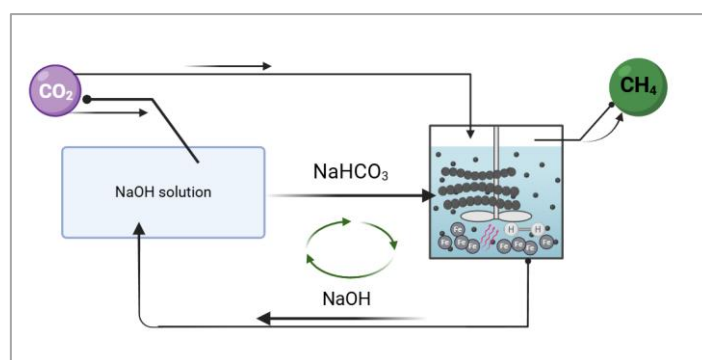


Figure 1: Schematic diagram of the system for the circular process using NaOH solution to absorb CO₂, promoting CO₂ utilization and maximizing the produced CH₄.

Material and methods

To assess the effect of reduced alkaline strength on CO₂ absorption and subsequent methanogenic activity, a 0.25 M NaOH solution was prepared and subjected to CO₂ flushing under controlled conditions. As previously discussed, CO₂ introduction promotes partial chemical formation of siderite (FeCO₃) from ZVI, impacting long-term reactivity.

Two ZVI dosing strategies were compared: one system received an initial dose of 50 g/L ZVI, while the second began with 10 g/L, followed by incremental additions of 10 g/L ZVI during each substrate re-feed. The initial pH was adjusted to 6.5. This setup aimed to evaluate whether a staggered ZVI addition could enhance CH₄ production and reduce passivation effects associated with siderite precipitation.

This methodological approach builds upon findings by Yoo et al. (2013), who demonstrated that NaOH solutions capture CO₂ through a two-step formation of Na₂CO₃ and NaHCO₃. Their results showed a strong dependence of CO₂ absorption rate on NaOH concentration, highlighting its relevance for controlled carbon dosing in bioreactor

systems. Their study highlighted that lower concentrations slow down initial absorption rates, potentially reducing efficiency but enabling finer control over CO₂ delivery and utilization within bioprocess systems. All tests were conducted under controlled ambient temperature, and each experimental condition was repeated in triplicate to ensure reproducibility

Results and discussion

The metal-bioprocess results presented in Figure 2 demonstrate that variations in the initial ZVI concentration significantly impact the rate of H₂ production, consequently affecting the final CH₄ yield. The setup with the ZVI concentration added entirely at the beginning proved to be more efficient in CH₄ production, maintaining its activity throughout the process. Conversely, the gradual addition of ZVI showed initial improvements in the system's performance but did not sustain these benefits across all 3 cycles.

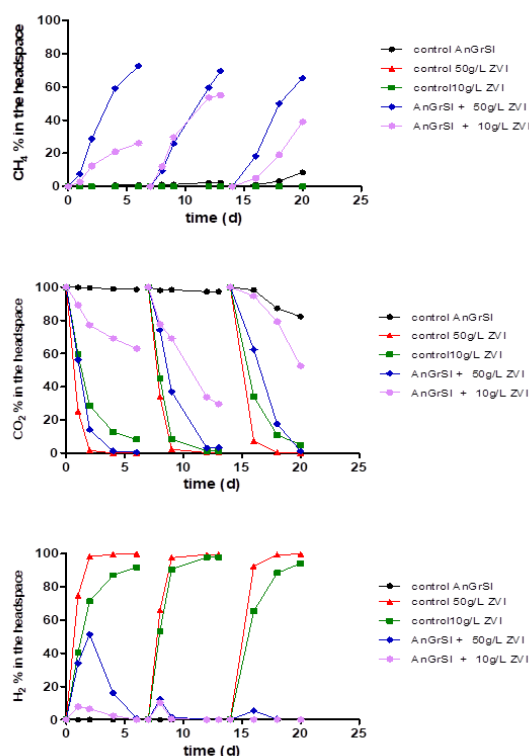


Figure 2: Gas composition over time in the gas phase in the presence of ZVI, AnGrSl, and CO₂ as a sole carbon source for ZVI concentration 50 g/L and initially 10g/L plus 3 additions of 10 g/L one in each cycle and NaOH flushed media (initial pH 6.5)

Conclusions

This study presents a low-energy, circular biogas upgrading strategy integrating CO₂ capture and biological methanation. The continuous regeneration of NaHCO₃ from NaOH promotes efficient carbon utilization and supports both circular economy principles and enhanced CH₄ yields under mild operational conditions.

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