Selective CO_2 absorption in bioreactors based on molecular modelling, thermodynamics, kinetics and experiments

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Highlights

- Advanced Methane Purification with MgO-$Mg(OH)_2$.
- 100% CO_2 Removal in 1 Day with S_2 Solution.
- Hybrid Strategy Cuts Processing Time by 1000%.
- Seamless Integration into Existing Bioreactors.

1. Introduction

Biogas, a renewable energy source composed of CO_2-CH_4 mixtures, offers an eco-friendly alternative to natural gas but requires effective CO_2 separation to enhance its heating value and reduce greenhouse gas emissions. Various techniques, including absorption, membrane, cryogenic separation, and adsorption, have been explored for CO_2-CH_4 separation. Among these, adsorption stands out for its simplicity, low cost, and operational flexibility. However, the economic viability of methods like photosynthetic bacteria systems is challenged by cultivation complexities. The study focuses on MgO-$Mg(OH)_2$ composites for their superior CO_2 adsorption capacity, despite the challenges posed by $MgCO_3$ shell formation that limits CO_2 diffusion. Inspired by the Namib Desert beetles' water-harvesting strategies, this research investigates structured combinations of MgO and $Mg(OH)_2$ to enhance CO_2 adsorption while minimizing CH_4 adsorption, due to the latter's weak interaction with $Mg(OH)_2$ surfaces. Employing both bulk thermodynamic and surface Density Functional Theory (DFT) modelling, the study initially simulates selective CO_2 absorption over CH_4, laying the groundwork for experimental validation. The experiments utilize biological (PNSB) and chemical (MgO-$Mg(OH)_2$ solutions and solid MgO powder) absorption agents in a pig farm's anaerobic fermentation bioreactor. By comparing biological and chemical methods against model predictions, the research validates the effectiveness of MgO-$Mg(OH)_2$ composites in CO2-CH_4 separation and proposes a synergistic approach that combines the rapid CO_2 removal of MgO-$Mg(OH)_2$ solutions with the bioresource recovery capabilities of PNSB.

2. Methods

This study combines theoretical and experimental approaches to examine CO_2 selectivity in biogas purification systems. Using FactSage for bulk thermodynamics and VASP for Density Functional Theory (DFT) calculations, we predicted CO_2 and CH_4 absorption capabilities of MgO and $Mg(OH)_2$. Theoretical models used temperature and pressure settings of 25°C and 1 ATM, respectively, and incorporated van der Waals forces in DFT to assess adsorption on MgO and $Mg(OH)_2$ surfaces. Lower adsorption energy values indicated stronger adsorption potential. Experimentally, high-purity chemicals and a specific PNSB mix were utilized in separation tests within bioreactors, involving heat sterilization and agitation at 150 rpm under controlled light conditions. Gas concentrations were measured using GC-TCD, with the goal of validating theoretical predictions on CO_2 selectivity in three systems, ranging from biological to chemical separation.

3. Results and discussion

Bulk thermodynamic calculations reveal that MgO and $Mg(OH)_2$ can absorb CO_2 effectively, with a 100% reaction rate in transforming into $MgCO_3$, while their reaction with CH_4 is negligible due to kinetic limitations and the formation of $MgCO_3$ shells that slow down CO_2 absorption. Surface DFT

calculations show MgO has a strong affinity for CO_2 with significant adsorption energy, suggesting strong physical adsorption, whereas CH4 exhibits weak adsorption on both MgO and $Mg(OH)_2$ surfaces due to minimal interaction, as indicated by the projected density of states (PDOS). The adsorption properties highlight MgO's stronger bond with CO_2 compared to $Mg(OH)_2$, suggesting an interwoven MgO/$Mg(OH)_2$ composite could enhance selective CO_2 capture over CH_4, mimicking the Namib Desert beetle's moisture collection mechanism. Measurements of selective CO_2 capture in different systems show dynamic CO_2 reduction in photobioreactors using biological (photosynthetic bacteria) and chemical (MgO solid powder) approaches. The introduction of MgO solid powder significantly reduces CO_2 levels while causing fluctuations in CH_4 concentration, aligning with DFT simulation predictions. The combined use of MgO and $Mg(OH)_2$ particles expedites CO_2 elimination compared to standalone biological or chemical methods, demonstrating a potential for simultaneous nutrient recovery and biogas upgrading from anaerobic digested wastewater. This integrated approach promises enhanced efficiency in separating CO_2 from CH_4, leveraging the strengths of both adsorption mechanisms and biological fixation to address methane purification challenges.

4. Conclusions

This study evaluates methane purification methods in anaerobic fermentation bioreactors, focusing on CO_2 absorption using chemical adsorbents and photo-synthetic bacteria (PNSB). Through a combination of modeling and experiments, we found that MgO and $Mg(OH)_2$ selectively capture CO_2, with surface modeling predicting excellent CO_2 selectivity for MgO-$Mg(OH)_2$ composites, confirmed by empirical data. PNSB reduced CO_2 by 40% in 10 days, whereas the S2 composite achieved complete CO_2 removal in one day without affecting methane levels, significantly outperforming both PNSB and S3, the latter preserving only 5% of CH_4. We propose a novel hybrid approach that transforming methane purification in bioreactors by enhancing efficiency and sustainability. This method, incorporating an adsorption module, can be easily integrated into existing systems, offering a practical solution for methane purification.

References

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Keywords

Bulk and Surface Modelling; Selective CO_2 Absorption; Methane Purification; Photosynthetic Bacteria (PNSB).