



Article Modelling Selective CO₂ Absorption and Validation via Photosynthetic Bacteria and Chemical Adsorbents for Methane Purification in Anaerobic Fermentation Bioreactors

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Abstract: This study delves into advanced methane purification techniques within anaerobic fermentation bioreactors, focusing on selective CO2 absorption and comparing photosynthetic bacteria (PNSB) with chemical adsorbents. Our investigation demonstrates that MgO-Mg(OH)₂ composites exhibit remarkable CO₂ selectivity over CH₄, substantiated through rigorous bulk and surface modelling analyses. To address the challenges posed by MgCO₃ shell formation on MgO particles, hindering CO₂ transport, we advocate for the utilisation of MgO-Mg(OH)₂ composites. In on-site experiments, these composites, particularly saturated MgO-Mg(OH)₂ solutions (S2), achieved an astonishing 100% CO₂ removal rate within a single day while preserving CH₄ content. In contrast, solid MgO powder (S3) retained a mere 5% of CH₄ over a 10 h period. Although PNSB (S1) exhibited slower CO₂ removal, it excelled in nutrient recovery from anaerobic effluent. We introduce a groundbreaking hybrid strategy that leverages S2's swift CO₂ removal and S1 PNSB's nutrient recovery capabilities, potentially resulting in a drastic reduction in bioreactor processing time, from 10 days when employing S1 to just 1 day with the use of S2. This represents a remarkable efficiency improvement of 1000%. This pioneering strategy has the potential to revolutionise methane purification, enhancing both efficiency and sustainability. Importantly, it can be seamlessly integrated into existing bioreactors through an additional CO_2 capture step, offering a promising solution for advancing biogas production and promoting sustainable waste treatment practices.

Keywords: bulk and surface modelling; $MgO-Mg(OH)_2$ composites; selective CO_2 absorption; methane purification; photosynthetic bacteria (PNSB); anaerobic fermentation bioreactors

1. Introduction

As a naturally occurring and renewable energy source, biogas, which consists mainly of carbon dioxide–methane (CO_2 - CH_4) mixtures, has emerged as an alternative fuel to natural gas. However, the presence of CO_2 can reduce the heating value and generate greenhouse gases. Therefore, the effective separation of CO_2 and CH_4 in biogas streams through targeted CO_2 reduction is critical for the practical application of biogas.

Various separation techniques have been developed to solve the problem, such as absorption, membrane separation, cryogenic separation, and adsorption [1]. While the photosynthetic bacteria system offers the advantage of simultaneous CO₂ capture and methane content enhancement [2], it is essential to acknowledge that its economic viability can be compromised by challenges in cultivation techniques [3,4]. The current materials and methods are less cost- and time-effective and should be redesigned based on this research finding.



Citation: Hsu, Y.-C.; Wu, S.; Chiu, J.-Y.; Thenuwara, H.N.; Senevirathna, H.L.; Wu, P. Modelling Selective CO₂ Absorption and Validation via Photosynthetic Bacteria and Chemical Adsorbents for Methane Purification in Anaerobic Fermentation Bioreactors. *Materials* **2023**, *16*, 6533. https://doi.org/ 10.3390/ma16196533

Academic Editors: Tamas Varga and Paula Teixeira

Received: 9 August 2023 Revised: 18 September 2023 Accepted: 28 September 2023 Published: 1 October 2023



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Adsorption is considered to be a competitive solution, and has the advantages of simple process, mild operating conditions, great operating flexibility, wide operating temperature range, low operating cost, stable performance, and no corrosion and fouling [4]. Currently, there are a number of experimental studies that provide good data for the adsorption of pure CO_2 or pure CH_4 on microporous materials, such as oxides [5,6], activated carbons [7,8], metal–organic framework materials [9,10], and zeolites [11,12]. However, the number of studies on the adsorption properties of the CO_2/CH_4 mixture is limited, although recent experimental studies show that selective adsorption of CO_2 is possible [13–18]. The theoretical simulation of the separation of CO_2 from CO_2/CH_4 mixtures by microporous MOFs by Bastin et al. [19], and adsorption behaviour of an equimolar CO_2/CH_4 mixture in carbon nanotubes (CNTs) by Huang et al. [20], show that the use of adsorption techniques is useful for the selective adsorption of CO_2 . The CNTs have the best selectivity for the binary CO_2/CH_4 mixture when the selectivity of common adsorbents like activated carbons, zeolites, MOFs, and others is compared [20]. The selective CO_2 adsorption capability of the adsorbent is the vital component for their industrial application.

Due to its substantial theoretical CO_2 capture capability (1100 mg CO_2/g adsorbent), MgO-based composites have been identified as a promising CO_2 absorbent. However, commercial MgO at 50 °C has a relatively low CO_2 adsorption capacity of 8.8 mg/g [21], whereas porous MgO produced by the thermal breakdown of $Mg(OH)_2$ has a 33 mg/g CO₂ removal capacity [22]. MgO particles react with CO_2 to create MgCO₃, which surrounds the unreacted MgO particles and prevents CO₂ molecule diffusion [6,23]. To overcome the carbonate blocking effect, we adopted water-harvesting strategies from a genus of Namib Desert beetles [24]. The Stenocara beetle's back is covered in many hydrophilic bumps that are not waxy and are surrounded by a hydrophobic wax-coated background. The alternate hydrophobic and hydrophilic surface domains promote water generation and adsorption. Recent research [25] has found that well-structured combinations of strong CO_2 adsorbents, like MgO, and weak CO_2 adsorbents, like Mg(OH)₂, can greatly increase the practical CO_2 adsorption capacity. The adsorption of CH₄ is anticipated to remain minimal due to the restricted interaction between CH_4 and the surface OH- group on the Mg(OH)₂ surface. The current study suggests using $MgO-Mg(OH)_2$ composite as chemical absorbents for CO_2 and CH_4 separation in biogas, in light of these insights. While admitting the inherent constraints in CH_4 adsorption brought on by the weaker interaction with the $Mg(OH)_2$ surface, the interweaving of both materials offers the possibility of increased CO_2 capture efficiency. Additionally, the use of CO_2 by microalgae or anaerobic photosynthetic bacteria is a rapidly expanding technology for energy conservation. In order to upgrade the methane gas produced by a pig farm, we conducted our research in photobioreactors employing purple non-sulphur bacteria (PNSB) and composite materials made of MgO-Mg(OH)₂ [26].

This study started by simulating the selective absorption of CO_2 over CH_4 by MgO-Mg(OH)₂ composites using both bulk thermodynamic and surface Density Functional Theory (DFT)-based modelling. The results from the modelling establish the groundwork for the later experimental validations. For validation purposes, both biological and chemical experimental methodologies were used. First, biological PNSB was introduced as an absorption agent (S1), which is renowned for its cutting-edge capabilities in wastewater treatment and bioresource recovery. The second method involves chemical absorption utilising two substances: an aqueous solution of $MgO-Mg(OH)_2$ (S2) and solid MgO powder (S3). On-site sampling was conducted at the anaerobic fermentation methane outlet of a pig manure solid–liquid separation-free bioreactor. Methane gas produced from the anaerobic fermentation of solid-liquid separated free livestock waste was passed through a desulphurization tower and subsequently injected into the bioreactor, allowing for a 10-day shaken culture experiment. To compare the adsorption effects of the biological and chemical techniques, variations in CO₂ and CH₄ were continually measured throughout the observation time. The findings of the experiments were compared to those predicted by the models, and both biological and chemical methods underwent careful analysis. In

the end, a synergistic strategy combining PNSB (S1) and MgO-Mg(OH)₂ aqueous solution (S2) is suggested.

2. Methodology

This study employs a combination of modelling prediction and experimental validation methods to investigate CO_2 selectivity in the S1, S2, and S3 systems.

2.1. Theoretical Calculations

For computer modelling, two techniques are utilised: (1) bulk thermodynamic calculations using the commercial software FactSage (Centre for Research in Computational Thermochemistry, Montreal, Canada) [27] and (2) DFT calculations using the Vienna ab initio simulation package (VASP) (VASP Software GmbH, Vienna, Austria) [28] with the Perdew–Burke–Ernzerhof (PBE) generalised gradient approximation (GGA) exchange– correlation functional [29].

2.1.1. Bulk Thermodynamic Calculations for CO_2 and CH_4 Absorption Using MgO and Mg(OH)₂, Respectively

In our thermodynamic modelling, we utilised the Equilib module from FactSage [27] to compute the chemical equilibria involving CO_2 (gas) and CH_4 (gas) in conjunction with MgO and Mg(OH)₂. The calculations incorporated thermodynamic data for all relevant compounds, as provided in the FactPS and FToxid databases. These calculations were conducted at a temperature of 25 °C and a pressure of 1 ATM.

2.1.2. DFT Calculations of CO2 and CH4 Absorption on MgO and Mg(OH)2 Surfaces

In order to investigate the surface absorption of CO₂/CH₄ on MgO and Mg(OH)₂, a projector augmented wave (PAW) method [30,31] was adopted as a plane-wave basis set to describe the electron–core interaction. The kinetic energy cutoff for the plane-wave expansion was set at 500 eV. The van der Waals contribution was taken into account using the DFT+D3 correction technique developed by Grimme et al. [32]. The total energy convergence was set as 1.0×10^{-6} eV, and the force on each individual atom was minimised to be smaller than 0.01 eV/Å for geometry optimisation and total energy calculations. The value for smearing was fixed to 0.01 eV. Monkhorst–Pack [33] K-points mesh was used for sampling the Brillouin zone, with the K-points number (N_K) being adjusted to keep (N_K × L) and with L being the lattice constant equal to ~45 Å for structural relaxations and ~75 Å for electronic calculations, respectively.

The previously published [34] optimised MgO and Mg(OH)₂ crystalline structures were used in this work. MgO and Mg(OH)₂ were both cleaved in the most stable (001) orientation in order to examine their adsorption of CO₂ and CH₄ [35,36]. To make sure that the interaction force between the layer planes was sufficiently small, the vacuum between them was 20 Å thick. MgO slabs are composed of six layers of the 3×3 expansion of the MgO unit cell. The adsorbate molecule and top 3 layers were free to relax, while the bottom 3 layers remained fixed in their bulk placements. Mg(OH)₂ slabs are composed of three layers of the 4×4 expansion of the Mg(OH)₂ unit cell. The adsorbate molecule and top two layers were free to relax while the bottom layer was held in its bulk position.

The adsorption energy E_{ad} of the adsorbate molecule X (X = CO₂ or CH₄) on the MgO and Mg(OH)₂ surface is defined as $E_{ad} = E_{surface+X} - E_X - E_{surface}$, where $E_{surface+X}$ is the total energy of the surface and adsorbate molecule, E_X is the energy of the adsorbate molecule CO₂ or CH₄, and $E_{surface}$ is the total energy of the surface. A lower value of E_{ad} denotes the stronger molecule's adsorption on the surface. The charge of an atom was defined as the difference between the valence charge and the Bader charge. The Bader charge was calculated using the Bader scheme of charge density decomposition [37,38].

2.2. Materials and Reagents

Chemicals with a purity of over 95% and 200 mL drip bottles with sealed caps were procured from Nihon Shiyaku Industries Ltd. (Osaka, Japan). The PNSB used in the study consisted of Rhodospirillum, Rhodopseudomonas, and Rhodomicrobium, which constitute the major microbial communities provided by the Food Research Institute. Rhodopseudomonas palustris makes up the majority of the bacterial communities among them. The components of the bacterial growth medium are detailed in Table 1.

Component	Yeast Extract	CH ₃ CH ₂ COONa	NH ₄ Cl	K ₂ HPO ₄	NaCl	MgSO ₄ •7H ₂ O	Concentrated Trace Salt Solution *
amount	10 g	100 g	2 g	2 g	1 g	0.4 g	50 mL

Table 1. Components of bacterial growth medium of 1 litre.

* Concentrated trace salt solution was prepared by mixing 50 mL of de-ionized water with 1 g of FeCl₃•6H₂O, 2 g of CaCl₂, 0.2 g of MnCl•4H₂O, and 0.1 g of Na₂MoO₄•2H₂O.

In our earlier study, we reported on the synthesis and characterisation of MgO-Mg(OH)₂ composites [25].

2.3. Separation Measurement of S1, S2, and S3 Systems, Respectively

Dry heat sterilisation was applied to a 200 cc drip bottle over the course of six hours in an oven set to 160 °C. Three different types of separation experiments were carried out in a SAN-C301 biological safety cabinet from San-Hsiung Technology Co., Ltd. (Kaohsiung City, Taiwan): (1) introducing S1, comprising 100 mL of PNSB liquid with a cell concentration of 106 cells/mL, into each of the five sterilised bottles or bioreactors, (2) introducing S2, consisting of 20 g of MgO powder and 100 mL of H₂O, into each of the five bioreactors, and (3) adding S3, including 20 g of magnesium oxide only, into each of the five bioreactors, once the bioreactors have cooled down. Three distinct types of bottles were agitated at 150 rpm, serving as photobioreactors for biogas purification. Subsequently, each of the five duplicate bottles was filled with gas via the methane vent from the Central Livestock Farm. Following this, each bottle was promptly sealed using a rubber stopper and secured with an aluminium cover. These bioreactors were then placed within a growth chamber set to maintain a temperature of 25 °C, operating under a 16/8 h light/dark cycle with a light intensity of 3000 lux.

To determine the concentrations of CO₂ and CH₄, we employed Shimadzu GC-8A GC-TCD (Shimadzu Scientific Instruments (Taiwan) Co., Ltd., Taipei City, Taiwan) equipped with a Shimadzu SUS column ($4 \times 3.0 \times 3.0$ m) packed with Porapax Q50/80 mesh material. The injection temperature, detector temperature, and oven temperature were set at 150 °C, with the oven temperature held at 45 °C. Helium served as the carrier gas. The concentration of CH₄ and CO₂ was determined using a calibration curve established via a standard gas mixture (55% CH₄, 20% CO₂, and 25% He) obtained from Jing De Gases Co., Ltd. (Kaohsiung City, Taiwan)

3. Results and Discussion

3.1. Bulk Thermodynamic Calculations

Table 2 calculates and summarises the chemical reactions for equilibrium CO_2 and CH_4 absorption in S2 and S3 systems. The calculated products, which might not be achieved because of unfavourable kinetics, are thermodynamic equilibrium products.

As can be observed from Table 2, when MgO reaches the equilibrium reaction with H_2O , it can completely transform into Mg(OH)₂, as shown in Equation (1). Equations (2) and (3) demonstrate that an equal amount of MgCO₃ was created by MgO and Mg(OH)₂ with a 100% reaction consuming the same amount of CO₂. However, neither MgO nor Mg(OH)₂ are anticipated to react with CH₄. Even though Equations (2) and (3) predict that MgO and Mg(OH)₂ can absorb 100% of the CO₂, kinetic restrictions may prevent their implementation. For instance, the production of MgCO₃ shells around the core MgO particles greatly

slows down the CO₂ absorption process [6]. Contrarily, physical adsorption attributed to structural advantages or electrostatic interaction may have a considerable impact, even though Equations (4) and (5) predict 0% CH₄ absorption by MgO and Mg(OH)₂. The following in-depth analysis of the surface absorption of CO_2/CH_4 on MgO and Mg(OH)₂ surfaces is therefore required.

Table 2. Calculated equilibrium reactions of CO₂ and CH₄ absorption using MgO and Mg(OH)₂.

Reactants		Products	
$MgO + H_2O$	->	$H_2O + Mg(OH)_2$	(1)
20.0 g 100.0 g	-/	91.1 g 28.9 g	(1)
$MgO + CO_2$	_\	$MgO + MgCO_3$	(2)
20.0 g 10.0 g	-/	10.8 g 19.2 g	(2)
$CO_2 + H_2O + Mg(OH)_2$	->	$H_2O + MgCO_3 + Mg(OH)_2$	(3)
10.0 g 91.1 g 28.9 g	-/	95.1 g 19.2 g 15.7 g	(3)
$MgO + CH_4$ 20.0 g 10.0 g =>		$MgO + CH_4$	(4)
		20.0 g 10.0 g	
$Mg(OH)_2 + H_2O + CH_4$	_>	$Mg(OH)_2 + H_2O + gas mixture (CH_4 + H_2O)$	(5)
28.9 g 91.1 g 10.0 g	->	28.9 g 90.8 g 10.3 g (10.0 g + 0.3 g)	(3)

3.2. Surface DFT Calculations

The optimised configurations for MgO and Mg(OH)₂ with adsorbed CO₂ and CH₄ are shown in Figure 1. The attractive/repulsive interaction between molecules was not taken into account when estimating the adsorption energy in this simulation because only one adsorbate molecule was introduced to the surface. According to our preliminary research, the adsorption energy of the adsorbate molecule on the top of the lattice oxygen of MgO (Figure 2a) was the highest among the four potential adsorption sites, i.e., the two-fold bridge, the four-fold hollow, on the top of the oxygen anion, and on the top of the magnesium cation. However, among the three potential adsorption sites—the two-fold bridge, the four-fold hollow, and the top of the hydrogen cation—the adsorbate molecule's adsorption energy was the highest on top of the four-fold hollow of Mg(OH)₂. This is consistent with earlier findings [39,40].



Figure 1. The optimised configuration of CO_2 or CH_4 adsorption on MgO or Mg(OH)₂ surface, respectively. (**a**) CO_2 on the MgO surface, (**b**) CH_4 on the MgO surface, (**c**) CO_2 on Mg(OH)₂ surface, and (**d**) CH_4 on Mg(OH)₂ surface. Green, red, blue and grey balls represent Mg, O, C and H atoms, respectively.



Figure 2. Projected density of states of MgO with adsorbed CO_2 (a) and Mg(OH)₂ with adsorbed CO_2 (b), respectively. O_M and O_S refer to the O of CO_2 and O of the adsorbent, respectively.

Table 3 lists the adsorption properties for CH_4 and CO_2 on the MgO and Mg(OH)₂ surface. MgO and Mg(OH)₂ exhibit strong and weak adsorption to CO_2 , respectively. The adsorption energy difference is 0.525 eV. Contrarily, CH_4 exhibits weak adsorption on both MgO and Mg(OH)₂. The adsorption energy difference is 0.015 eV. This means that MgO has a strong attraction to CO_2 , while Mg(OH)₂ has a mild one. An interwoven composite with alternate layers of MgO and Mg(OH)₂ is anticipated in order to improve CO_2 adsorption, which employs a mechanism similar to that of the Namib Desert beetle. Additionally, a composite comprised of MgO and Mg(OH)₂ would have little impact on the adsorption of CH_4 because of CH_4 's modest affinity for both of these substances. This suggests that CO_2 and CH_4 in the biogas might be separated.

A 1 1	E _{ad}	(eV)	Charge		
Adsorbate	MgO	Mg(OH) ₂	MgO	Mg(OH) ₂	
CH ₄ CO ₂	$-0.173 \\ -0.727$	$-0.158 \\ -0.202$	0.02 0.40	0.00 0.01	

Table 3. Adsorption properties for CH₄ and CO₂ on MgO and Mg(OH)₂.

The distance from CO_2 to the MgO surface is shown in Figure 1; it is 1.517, which is more than the C-O bond length of 1.43 mm [41]. This demonstrates that the adsorbed CO₂ does not chemically react with MgO to form carbonate; therefore, the adsorption can be assumed to be strong physical adsorption. Since the distance between CO_2 and the Mg(OH)₂ surface is significantly longer than the length of the C–O bond, it is likely due to weak physical adsorption. CH₄ is farther away from MgO and Mg(OH)₂ surface than CO₂. Perhaps the steric effect is involved here. This agrees with the average angle depicted in Figure 1. The average H–C–H angle of CH_4 changes from 109.5° to 109.4° on the Mg(OH)₂ surface and 109.0° on the MgO surface, respectively, indicating the stiffness of the CH₄ molecule. On the other hand, the C–O–C angle of CO_2 changes from 180.0° to 179.0° on the Mg(OH)₂ surface and 133.6° on the MgO surface. This proves that MgO highly polarises the CO_2 molecule. Table 3 shows that the CO_2 molecule accepts a charge of 0.40, indicating that MgO donated 0.40 electrons to the CO_2 molecule. The CO_2 may become polarised as a result of MgO's transfer of electrons to it. The fact that MgO and Mg(OH)₂ both gave very few electrons to CH₄ molecules points to a weak interaction with the surface. As a result, CH_4 can be regarded as being weakly physically adsorbed by MgO and Mg(OH)₂.

Figure 2 displays the projected density of states (PDOSs) of the atoms for CO₂adsorbed MgO and Mg(OH)₂. The significant hybridisation between the O of CO₂ and Mg of MgO, as well as between the C of CO₂ and O of MgO, is observed in Figure 2a. The peaks of the PDOSs for the two atoms overlap between -5.0 and 0 eV. The strong hybridisation stabilises the CO₂ molecule on the MgO surface. There is also hybridisation between the O of Mg(OH)₂ and the C of CO₂ since their PDOSs share some peaks. However, as can be seen in Figure 2b, the overlap is slight. Therefore, the weak hybridisation results in a low adsorption energy of CO₂ on the Mg(OH)₂ surface. Figure 3 depicts the PDOSs of CH_4 -adsorbed MgO and Mg(OH)₂. Because the PDOSs of MgO or Mg(OH)₂ and CH_4 do not have any common peaks, this indicates that no appreciable hybridisation occurs between the atoms of either MgO or Mg(OH)₂ and the CH₄ molecule. As a result, the CH₄ molecule has poor adsorption on both the MgO and Mg(OH)₂ surfaces.



Figure 3. Projected density of states of MgO with adsorbed CH_4 (a) and Mg(OH)₂ with adsorbed CH_4 (b), respectively. H_M and H_S refer to the H of CH_4 and H of the adsorbent, respectively.

In conclusion, the adsorption energies computed in Table 3 match the trends discovered by FactSage computations, providing more nuanced understandings: (1) CO₂ exhibits stronger adsorption (-0.727 eV) than CH₄ (-0.173 eV) on the MgO surface. MgO does absorb CH₄, according to the surface model, contrary to Equation 4 in the bulk model. (2) The Mg(OH)₂ surface exhibits the same trend (-0.202 eV for CO₂ and -0.158 eV for CH₄) as the bulk model. (3) In contrast to what is implied by the bulk model, CH₄ forms a slightly stronger bond on MgO (-0.173 eV) than on Mg(OH)₂ (-0.158 eV). (4) MgO exhibits a much stronger bond with CO₂ (-0.727 eV) than Mg(OH)₂ (-0.202 eV). According to these results, the interweaving of MgO and Mg(OH)₂ structures may increase the effectiveness of selective CO₂ capture relative to CH₄.

3.3. Measurements of Selective CO₂ Capture over CH₄ in S1, S2, and S3 Systems

The dynamic changes in CO₂ concentration seen in photobioreactors are shown in Figure 4 using biological S1 and chemical S2/S3 approaches. Over a 10-day period at 150 rpm, S1 (photosynthetic bacteria) and S3 (MgO solid powder) consistently reduce CO₂ concentration, while S2 completely eliminates CO₂ on the first day. Figure 5 displays changes in the observed CH₄ concentration over time in photobioreactors. S1 and S2 both show a negligible drop in CH₄ during a 10-day period at 150 rpm. However, S3 (the introduction of MgO solid powder in the photobioreactor) causes the CH₄ reduction to fluctuate, which is consistent with the results of our DFT simulation shown in Table 3 (-0.173 eV for CH₄/MgO adsorption). The simulation indicates that the adsorption energy of CH₄ on the MgO surface is stronger than that of CH₄ on Mg(OH)₂, providing an explanation for the observed fluctuations in CH₄ concentration when MgO solid powder is solely added. The abundant MgO surface sites in S3 contribute to the varying CH₄ concentration.

Additionally, the CO₂-phobic (Mg(OH)₂) and CO₂-philic (MgO) model [25,34], which is modelled after the water collection system used by the Namib Desert beetle [24], is responsible for the quick elimination of CO₂ through the use of S2, where MgO-Mg(OH)₂ particles are used due to metastable chemical equilibrium, as in the current study, the solubility of MgO is 0.0086 g/100 mL at 30 °C. We did not look at the early phases of the reaction because the effectiveness of our suggested method for purifying methane was the focus of our work. Neshat et al. [2] only observed a slight reduction in CO₂ levels after three days and a 10% decline after ten days when employing purple photosynthetic bacteria for CO₂ fixation from biogas, a significantly slower process compared to our combined approach utilising photosynthetic bacteria and adsorption.



Figure 4. Variation in CO₂ concentration with time during purification and under shaking at 150 rpm. S2 (•), S3 (\blacksquare), and S1 (\blacklozenge).



Figure 5. Variation in CH₄ concentration with time during purification and under shaking at 150 rpm. S2 (\bullet), S3 (\blacksquare), and S1 (\blacklozenge).

In contrast to adsorbents that are only utilised for methane purification, PNSB demonstrated the potential for concurrent nutrient recovery and biogas upgrading from anaerobic digested wastewater. The S2 method and S1 for waste water treatment and resource recovery can be coupled to expedite the CO_2 separation from CH_4 process.

4. Conclusions

This study presents a comprehensive analysis of methane purification in anaerobic fermentation bioreactors, with a particular emphasis on selective CO_2 absorption. We systematically evaluated the efficacy of chemical adsorbents (S2 and S3) and photosynthetic bacteria (PNSB) for CO_2 capture and methane purification, employing a combination of modelling and experimental techniques.

Our investigation initially demonstrated the selective CO_2 over CH_4 behaviour in MgO and Mg(OH)₂ systems through bulk thermodynamic equilibrium modelling. Al-

though it could not predict CH_4 absorption on MgO, the surface DFT modelling results confidently predicted excellent CO_2 selectivity for MgO-Mg(OH)₂ composites, a prediction substantiated by on-site measurements.

PNSB (S1) exhibited commendable CO_2 removal, achieving a 40% reduction over 10 days. In contrast, the S2 (MgO-Mg(OH)₂ composite) showed remarkable speed, achieving complete CO_2 removal within a single day while retaining 100% of the original CH₄ content in the biogas. In contrast, S3 (solid MgO powder) was less effective, preserving only 5% of CH₄ after a 10 h reaction. Consequently, S2 demonstrated an unparalleled CO_2 removal speed, outperforming PNSB by a factor of 10.

Drawing from these results, we propose an innovative hybrid method that leverages the rapid CO_2 removal capability of S2 and the superior nutrient recovery attributes of S1 PNSB. This approach holds the potential to revolutionise methane purification in anaerobic fermentation bioreactors, enhancing both efficiency and sustainability. Moreover, it can be seamlessly integrated into existing bioreactors with the addition of an adsorption module, making it highly practical.

Author Contributions: Y.-C.H.: experiments and data collection. S.W.: draft manuscript, DFT model, figures, data collection, literature review. J.-Y.C.: design experiments, conceptualisation, methodology, supervision, draft revision. H.N.T.: sample preparation, data collection, literature review. H.L.S.: FactSage calculations, software, editing figures and manuscript, data collection, literature review. P.W.: conceptualisation, methodology, supervision, draft manuscript, funding acquisition. All authors have read and agreed to the published version of the manuscript.

Funding: This research is funded by the Agency for Science, Technology and Research (A*STAR) (Singapore), under the AME Individual Research Grant (award no. A20E7c0108), the Ministry of Education (Singapore), under the tier 2 programme (award no. MOE2018-T2-1-163), and the Singapore University of Technology and Design (SUTD) Kickstarter Initiative (SKI) programme, under award number SKI 2021_02_15.

Data Availability Statement: The datasets used and/or analysed during the current study are available from the corresponding author upon reasonable request.

Acknowledgments: We acknowledge the support provided by the Agency for Science, Technology and Research (A*STAR) (Singapore), under the AME Individual Research Grant (award no. A20E7c0108), the Ministry of Education (Singapore), under the tier 2 programme (award no. MOE2018-T2-1-163), and the Singapore University of Technology and Design (SUTD) Kickstarter Initiative (SKI) programme, under award number SKI 2021_02_15. Additionally, we extend our gratitude to the CRCT of the University of Montreal, Canada, for providing the FactSage software, which was instrumental in conducting this research.

Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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