Green Chemistry

TUTORIAL REVIEW

View Article Online
View Journal | View Issue

Cite this: *Green Chem.*, 2025, **27**, 1331

A comparative review of biohydrogen and biomethane production from biowaste through photo-fermentation

Dandan Xie,[a] Lingfen Kong,[a] Jiehua Hu,[a] Heng Li *[a,b] and Yuanpeng Wang *[b]

Given the depletion of fossil fuels and the environmental issues they cause, the search for alternative, clean, and renewable energy sources has made significant progress. Among them, the photo-fermentative production of bioenergy stands out as an attractive and environmentally friendly approach. This review comprehensively examines the key biological and technological characteristics and mechanisms involved in the production of biohydrogen and biomethane through photo-fermentation. Specifically, it discusses the use of wastewater or biowaste as feedstocks for photobiological hydrogen production, key factors influencing biohydrogen yields, and various enhancement methods. Building on the insights gained from biohydrogen production, we further explore the processes, methods, and mechanisms for enhancing photo-fermentative biomethane production areas that have not been thoroughly reviewed elsewhere. By linking biohydrogen and biomethane production, this study underscores the complementary roles of these bioenergy sources within a unified photo-fermentative framework. Additionally, it offers a comparative analysis of biohydrogen and biomethane in terms of mechanisms, feedstock utilization, environmental impact, economic viability and efficiency. The aim is to highlight recent advancements in this field, identify challenges and future perspectives, and discuss the potential of photobiological biohydrogen and biomethane as sustainable bioenergy sources.

Received 29th November 2024,
Accepted 23rd December 2024

DOI: 10.1039/d4gc06079b

rsc.li/greenchem

Green foundation

1. This review discusses advancements in the photo-fermentative production of biohydrogen and biomethane, emphasizing the use of biowaste and wastewater as feedstocks. It highlights improvements in microbial processes, bioreactor design, and energy efficiency, offering a cleaner, more sustainable alternative to traditional energy production methods, in line with green chemistry principles of waste reduction, resource efficiency, and environmental sustainability.
2. This review compares biohydrogen and biomethane production *via* photo-fermentation, highlighting key mechanisms, feedstock utilization, and their environmental and economic impacts. It emphasizes their complementary roles as sustainable bioenergy sources.
3. Future research will focus on optimizing processes for greater efficiency and scalability. This review provides essential insights that can guide the development of more sustainable bioenergy systems, advancing green chemistry and renewable energy solutions.

1. Introduction

The ever-growing energy demand and the resulting environmental challenges underscore the urgent need for sustainable and renewable energy sources.[1,2] Bioenergy, produced from organic materials like wastewater and biowaste, has emerged as a promising alternative.[3] Utilizing these waste materials not only mitigates environmental pollution but also provides a cost-effective energy production solution, aligning well with global efforts to combat climate change. Recognizing its potential to significantly enhance energy security, environmental

[a]*School of Marine Biology, Xiamen Ocean Vocational College, Applied Technology Engineering Center of Fujian Provincial Higher Education for Marine Resource Protection and Ecological Governance, Xiamen Key Laboratory of Intelligent Fishery, Xiamen 361100, China. E-mail: liheng310@foxmail.com*
[b]*Department of Chemical and Biochemical Engineering, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, P. R. China. E-mail: wypp@xmu.edu.cn*

sustainability, and economic growth, governments, industries, and research institutions are heavily investing in the development of efficient technologies for bioenergy production from various wastes. This shift towards bioenergy is crucial for creating a sustainable future and reducing dependence on conventional energy sources.

Bioenergy production from wastewater and biowaste involves two primary approaches: thermochemical and biochemical conversion.[4] Traditional thermal catalysis, despite being effective in accelerating bioenergy production, has drawbacks such as high energy demands. Therefore, the elevated temperature and pressure requirements in traditional thermal catalysis increase operational costs, while producing massive harmful by-products.[5] One of the key alternative techniques for converting wastewater or biowaste into bioenergy is adopting biochemical conversion, which includes anaerobic digestion, microbial fuel cells, and photo-fermentation.[6] Among them, photo-fermentation is particularly promising for converting organic substrates into hydrogen gas by using photosynthetic bacteria and light.[7] This process enables clean bioenergy production under mild conditions, with a wide range of wastewater and biowaste sources available, offering a more sustainable approach compared to traditional thermal methods.[4] Operating under ambient conditions, photo-fermentation reduces energy consumption and costs and minimizes the generation of harmful by-products, making it a more environmentally friendly and efficient alternative.

Despite its promise, the practical application of photo-fermentation is currently constrained by technical and economic challenges, necessitating ongoing research and technological advancements to enhance efficiency, reduce costs, and improve scalability. Several reviews have discussed biohydrogen production through photo-fermentation, focusing on reviewing the use of different photo-nanocatalysts[8] and nanomaterials,[9,10] and the challenges and advancements of algae based biofuels[11,12] and food waste.[13] However, such reported reviews largely concentrate on biohydrogen, with another important bioenergy source of biomethane being frequently ignored. In contrast, our review uniquely comments on the photo-fermentation production of both biohydrogen and biomethane from wastewater as well as biowaste. Unlike biohydrogen production, which is a direct process where light energy directly drives the production of hydrogen through photobiological reactions, biomethane production *via* photo-fermentation occurs through an indirect mechanism. Specifically, light energy stimulates the anaerobic degradation of organic matter, releasing electrons in the process. These electrons are then transferred through various biochemical pathways in an anaerobic environment.[14] A critical step in this process involves methanogenic archaea, which play a key role in converting intermediate compounds, such as acetate and hydrogen, into biomethane. This indirect mechanism involves a complex network of microbial interactions, distinguishing biomethane production from the direct, light-driven hydrogen production process.

This review, to the best of our knowledge, is the first one to systematically summarize recent advancements regarding photo-fermentative production of biomethane from wastewater and biowaste. The general structure of this review is illustrated in Fig. 1. In detail, we present a comparative analysis of biohydrogen and biomethane production in terms of mechanisms, feedstock utilization, environmental impact, economic assessment and waste-to-energy conversion efficiency, offering a comprehensive perspective on the potential of these bioenergy sources. As a result, this review offers valuable insights into

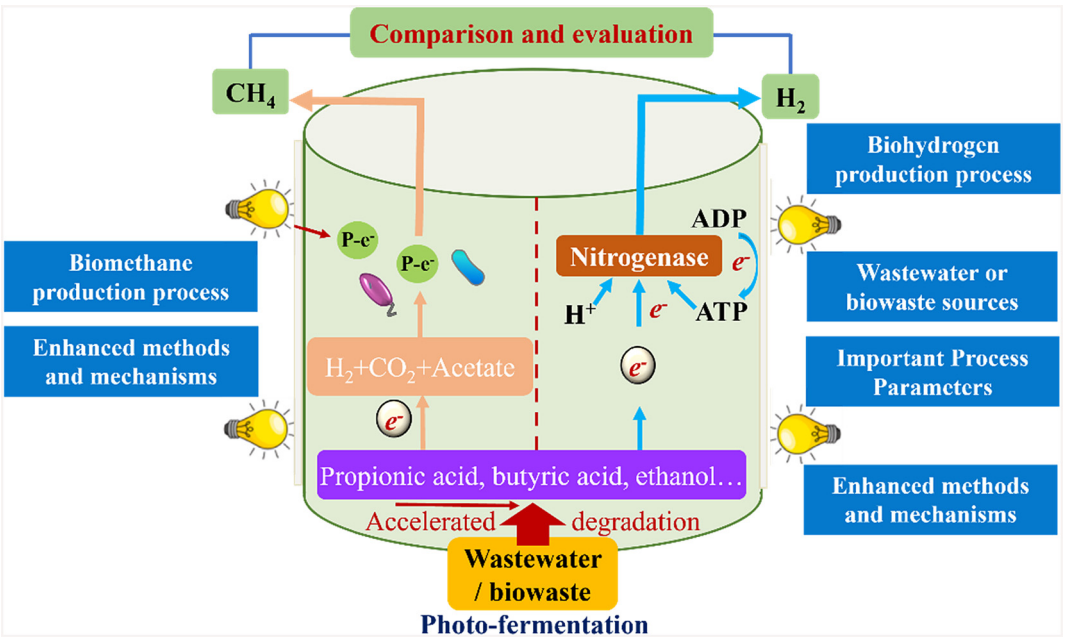

Fig. 1 The general information and structure of bioenergy production from wastewater and biowaste through photo-fermentation.

the potential of exploring the photo-fermentative approach for producing biohydrogen and biomethane as sustainable bioenergy sources, aligning well with the principles of green chemistry, namely promoting efficient waste utilization, minimizing environmental impact, and advancing renewable energy research and waste management practices.

2. Hydrogen production through photo-fermentation

2.1 Description of the process

Photo-fermentation is a biological process in which photosynthetic bacteria, particularly purple non-sulfur bacteria (PNSB), convert organic substrates from wastewater or biowaste into hydrogen gas (Fig. 2). These bacteria are adept at utilizing light energy to drive hydrogen production, a process that integrates metabolic and photosynthetic pathways.

The process begins with the introduction of organic substrates—such as carbohydrates, proteins, and fats—into a bioreactor where PNSB are cultured. These organic compounds serve as electron donors, which are metabolized by the bacteria to release electrons and protons, fundamental components in hydrogen production. A key feature of PNSB is their photosynthetic apparatus, which captures light energy, typically from sunlight or artificial light sources. Upon absorption, light energy excites electrons within the photosynthetic reaction center. These high-energy electrons are transferred through a membrane-bound electron transport chain, a sequence of proteins embedded within the bacterial membrane. During the electron transport process, protons are pumped across the membrane, establishing a proton gradient (proton motive force). This gradient is harnessed by ATP synthase, a membrane enzyme complex, to synthesize adenosine triphosphate (ATP). ATP provides the energy necessary for various cellular functions, including the reduction of protons to molecular hydrogen *via* the activity of hydrogenase enzymes.

The overall process can be summarized as the conversion of organic substrates into hydrogen gas, carbon dioxide, and other metabolic byproducts. Table 1 illustrates commonly used photosynthetic bacteria in photo-fermentation, including PNSB species like *Rhodobacter sphaeroides* and *Rhodopseudomonas palustris*.[15] Additionally, studies have explored the synergistic effects of combining multiple photosynthetic bacteria species to enhance hydrogen production. In this process, photosynthetic bacteria effectively harness solar energy to power the metabolic pathways that break down complex organic compounds. By converting waste-derived organic substrates into clean hydrogen fuel, this technology provides a sustainable approach for bioenergy production while promoting efficient degradation of waste materials.

2.2 Different wastewater and biowaste sources

The photo-fermentation production of hydrogen utilizes various wastewater and biowaste sources, each offering unique advantages due to their discrepant organic contents. Industrial wastewater, particularly from the food and beverage,[16–20] dairy,[21] and oil industries,[22] is rich in organic compounds such as sugars, fats, and proteins. These nutrients provide an excellent substrate for photosynthetic bacteria, rendering industrial wastewater a valuable source for hydrogen production.

The data presented in Table 1 highlight the variability of hydrogen bio-produced using different feedstocks and under varied operational conditions, emphasizing the importance of tailoring fermentation conditions according to the specific characteristics of each wastewater. Tofu wastewater, for instance, achieved a relatively high yield of biohydrogen up to 4.32 L L^{-1}, likely due to its rich nutrient content, including organic compounds such as amino acids, which support the growth and metabolic activity of the glutamine auxotrophic mutant of *Rhodobacter sphaeroides* in biohydrogen production.[20] Similarly, dairy wastewater demonstrated a high biohydrogen yield of 3.62 L L^{-1}, showcasing its potential as a rich substrate source.[21] This high yield may be due to its balanced

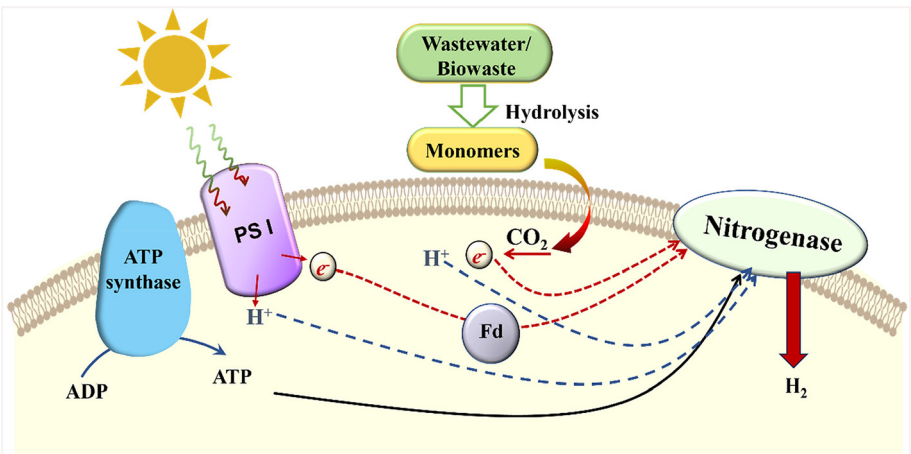

Fig. 2 Mechanism diagram of photo-fermentative biohydrogen production.

Table 1 Overview of studies related to biohydrogen production from wastewater and biowaste through photo-fermentation

Feedstock	Inoculum	Reactor	Light intensity source	Temp. (°C)	pH	H_2 yields	H_2 production rates	Ref.
Sugar refinery effluent and malic acid	*R. sphaeroides* O.U. 001	Batch	200 W m^{-2}	30	7	4.63 L L^{-1}	27.74 mL L^{-1} h^{-1}	16
Sugar wastewater	*Rhodobacter sphaeroides*	CSTR	7500 Lux	25.6	7	2.61 L L^{-1}	5.24 mL L^{-1} h^{-1}	17
Brewery wastewater	*Rhodobacter sphaeroides*	Batch	116 W m^{-2}	28 ± 2	7–7.2	2.24 L L^{-1}	61 mL L^{-1} h^{-1}	18
Soy sauce wastewater	*Rhodobium marinum*	Batch	60 W m^{-2}	30	7	2.67 L L^{-1}	38.14 mL L^{-1} h^{-1}	19
Tofu wastewater	*Rhodobacter sphaeroides*	Batch	6000–7000 Lux	30	7	4.32 L L^{-1}	—	20
Dairy wastewater	*Rhodobacter sphaeroides* O.U. 001	Batch	9000 Lux per (Hg W lamp)	28 ± 2	7–7.2	3.62 L L^{-1}	56 mL L^{-1} h^{-1}	21
Olive mill wastewater	PNSB	Batch	74 W m^{-2}	30 ± 0.2	6.8–7.2	1.03 L L^{-1}	5.87 mL L^{-1} h^{-1}	22
Mixture of restaurant/ brewery effluents	*Rhodobacter sphaeroides* DSM 158	Batch	126 W m^{-2}	30 ± 2	7	0.95 L L^{-1}	—	23
Dark fermented effluent and palm oil mill effluent	Indigenous bacteria	Batch	4500 Lux	30	7	1.64 L L^{-1}	18.65 mL L^{-1} h^{-1}	24
Brewery wastewater and pulp and paper mill effluent	PNSB	Batch	7000 Lux	30	7	15.46 L L^{-1}	717.57 mL L^{-1} h^{-1}	25
Wastewater of palm oil and effluents from the paper and pulp industries	*Rhodobacter sphaeroides* NCIMB8253	Batch	7000 Lux	30	7	8.72 L L^{-1}	763 mL L^{-1} h^{-1}	26
Bread waste	*Rhodobacter sphaeroides*	CSTR	40 W m^{-2}	25–28	6.8	—	1.96 ± 1.6 mL L^{-1} h^{-1}	27
Vegetable waste	*Rhodopseudomonas palustris*	Batch	35 μmol photons m^2 s^{-1}	30	6.8	—	9.6 ± 2.6 mL L^{-1} h^{-1}	28
Potato residue	*Rhodobacter sphaeroides* O.U. 001	Custom-designed bioreactor	LED bulb (20 W each)	30	7	6.31 mol (mol carbohydrate)$^{-1}$	—	29
Corncob	HAU-M1	Batch	3000 Lux	30	7	51.96 mL (g TS)$^{-1}$	—	30
Agricultural waste	Mixed bacterial strains HAU-M1	Batch	7000 Lux	30	7	84.7 mL (g TS)$^{-1}$	23.97 mL h^{-1}	31
Corn stover	HAU-M1	Batch	3500 Lux	30	6.5	141.42 mL (g TS)$^{-1}$	—	32
Corn stalk	*Rhodospirillum rubrum*	Batch	3000 Lux	30	6.5	119.3 mL g^{-1}	23.96 mL h^{-1}	33

composition of carbohydrates and proteins, which are readily metabolized by *Rhodobacter sphaeroides*. On the other hand, olive mill wastewater exhibited a significantly lower biohydrogen yield of 1.03 L L^{-1}, likely due to its relatively high polyphenol content, which inhibits microbial activity.[22] Such findings underscore the critical roles of substrate composition in influencing the metabolic activity of photosynthetic bacteria. In another case, a low biohydrogen yield of 0.95 L L^{-1} is primarily due to the absence of a specialized growth medium, although not using a medium can reduce cost and simplify the process by utilizing natural effluents as a nutrient source.[23] Additionally, the role of indigenous bacteria in the dark fermented effluent and the palm oil mill effluent is noteworthy, enabling a hydrogen yield of 1.64 L L^{-1} to be achieved, even without the use of specific inoculum strains.[24] This highlights the importance of leveraging naturally existing microbial communities in certain types of wastewater to reduce operational costs associated with inoculum preparation.

The comparison regarding hydrogen production between batch and continuous stirred-tank reactor (CSTR) systems in Table 1 also reveals the significance of process optimization. For instance, sugar wastewater treated in a CSTR achieved a biohydrogen yield of 2.61 L L^{-1}.[17] Although the biohydrogen production value is modest, this result implies the capacity of a continuous system to sustain stable hydrogen production over extended periods. The aforementioned analyses suggest that the optimization of reactor design and operational parameters (*e.g.*, light intensity and retention time) could enhance the yield of biohydrogen.

Co-fermentation of mixed wastewater in the photo-fermentation process can enhance hydrogen production yields. For instance, Hay *et al.* demonstrated that combining brewery wastewater with the pulp and paper mill effluent significantly boosted biohydrogen production.[25] The unique characteristics of brewery wastewater, such as its rich organic content and favorable C/N ratio, contribute to a higher hydrogen yield when used as a co-substrate in the photo-fermentation process. This synergistic effect not only optimizes the substrate utilization but also improves the overall efficiency and sustainability of biohydrogen production from industrial wastewater mixtures.

Biowaste, including agricultural residues and food waste, is another promising feedstock for bioenergy production through photo-fermentation. Biowaste derived from food processing and kitchen waste (Table 1) demonstrates significant potential for hydrogen production, due to its high organic content and biodegradability. An example of processing bread waste in a CSTR in the presence of *Rhodobacter sphaeroides* attained a hydrogen yield of 1.96 mL L^{-1} h^{-1},[27] while vegetable waste treated with *Rhodopseudomonas palustris* yielded a higher hydrogen production performance of 9.6 mL L^{-1} h^{-1} under batch conditions.[28] This suggests that vegetable waste, with its complex organic composition, supports higher hydrogen production compared to bread waste. In addition, research on custom-designed bioreactors for photo-fermentation hydrogen production shows that optimizing key process parameters can significantly enhance hydrogen yield, paving the way for scaling up from laboratory to commercial production.[29] These examples signify that food waste can serve as an effective substrate for photosynthetic bacteria, which enable the conversion of organic materials into hydrogen and concurrently address the dual challenges with regard to managing food waste and producing renewable energy. By optimizing fermentation conditions and reactor designs, the valorization of food waste can be further expedited to provide more solutions to obtaining sustainable energy.

Agricultural residues, such as straw, corn stover, and wood chips, contain lignocellulose, which can be pretreated and hydrolyzed to release fermentable sugars.[7] These sugars serve as substrates for photosynthetic bacteria to produce hydrogen. In addition, the summarized hydrogen production values (51.96–141.42 mL (g TS)$^{-1}$) listed in Table 1 also indicate that different agricultural residues exhibit diverse hydrogen yields, due to the differences in their compositions, pretreatment methods, and operational parameters. In the presence of HAU-M1, for instance, agricultural waste enabled the production of a notable hydrogen yield of 84.7 mL (g TS)$^{-1}$ under batch conditions, showcasing its suitability as a substrate stemming from its rich fermentable carbohydrates.[31] Similarly, corn stover demonstrated a remarkable hydrogen yield of 141.42 mL (g TS)$^{-1}$, attributed to its lignocellulosic structure, which provides ample fermentable sugars upon hydrolysis.[32]

In consideration of wastewater and biowaste, both are promising feedstocks for bioenergy production through photo-induced fermentation; however, differences exist. Notably, wastewater is abundant and cost-effective for large-scale applications, although its complex compositions and potential toxicities require careful management. Biowaste, renowned for its rich organic content, supports efficient nutrient recycling but may face challenges such as variability and microbial competition. Consequently, the selection of feedstock for hydrogen production depends on factors like availability, cost, and environmental impact, with such factors being examined beforehand to make wastewater treatment facilities and agricultural areas ideal for long-term and profitable bioenergy manufacturing. By utilizing these waste resources, photo-fermentation not only enables the production of renewable hydrogen but also helps reduce waste as well as support environmental sustainability.

2.3 Important process parameters

The efficiency of hydrogen production through photo-fermentation is influenced by several critical process parameters. Understanding and optimizing these parameters are essential for maximizing hydrogen yield.

Light intensity and wavelength are crucial to the activity of photosynthetic bacteria, primarily PNSB. Specifically, light intensity significantly influences the growth and biomass production of photosynthetic bacteria in wastewater treatment processes.[34] Optimal light intensity ensures maximum absorption and utilization of light energy, thereby enhancing the hydrogen production rate. Uyar *et al.* highlighted that the efficiency of hydrogen production in photobioreactors was significantly influenced by light conditions.[35] This study also emphasized that the illumination protocol, including continuous *versus* intermittent light exposure, played a key role in optimizing energy efficiency and enhancing hydrogen production rates. Noteworthily, different wavelengths can selectively stimulate or inhibit specific metabolic pathways, thereby influencing overall hydrogen output. However, excessive high light intensities can cause photoinhibition, giving rise to reduced bacterial activity.[34]

Beyond the light source, temperature also affects the metabolic activities of photosynthetic bacteria considerably. For example, the bioconversion process can occur under various temperature conditions: psychrophilic (0–25 °C), mesophilic (25–45 °C), thermophilic (45–65 °C), and hyperthermophilic (above 80 °C). It is important to note that temperature will interfere with metabolic pathways; therefore, optimizing enzyme activity within its specific temperature range is of crucial importance to biohydrogen production.[36] Within this temperature range, enzymatic activities and bacterial growth rates reach their maxima. As expected, temperatures outside this range can slow down metabolic processes or denature essential enzymes, in turn reducing hydrogen production efficiency. As is well known, anaerobic processes are highly temperature-dependent; as a consequence, the optimal pH required for different bacterial species can vary. For instance, the optimal temperature range for PNSB is 25–35 °C,[37] while some cyanobacterial strains can even thrive at thermophilic temperatures, such as 55 °C.[38]

Additionally, the pH level of the culture medium impacts bacterial growth, determining the performance of hydrogen production. The optimal pH for photo-fermentation is usually around neutral (pH 7.0); hence, deviations from this optimal pH can disrupt the stability and functionality of enzymes involved in hydrogen production. Maintaining a stable pH value is crucial for ensuring consistent bacterial activity and hydrogen output. However, controlling the pH value in these processes is highly challenging due to the presence of organic acids, such as the byproducts of volatile fatty acids. Acidification caused by such byproducts engenders a decrease

in the pH within the reactor over time, leading to a loss of buffering capacity in the system.[39] In a study, Guo *et al.* focused on using phosphate buffer to stabilize pH levels, leading to biohydrogen production improvement during photo-fermentation.[40] This finding confirms that the use of phosphate buffer can effectively maintain stable pH values throughout the entire fermentation process, which is crucial for ensuring that the photo-fermentation systems show excellent performance. By adopting phosphate buffer to inhibit significant pH fluctuations, the microbial activity in the photo-fermentation system is well preserved, in turn demonstrating a higher biohydrogen yield.

The availability of nutrients such as carbon, nitrogen, and trace elements is vital to bacterial metabolism. Organic substrates in wastewater provide the key carbon sources, while the existence of nitrogen is essential for protein synthesis and cell growth. Clearly, an appropriate balance between these nutrients imparts optimal bacterial activity, and excessive or deficient nutrient levels can result in suboptimal hydrogen production rates. As a consequence, the C/N ratio is a critical factor to be considered when using photo-fermentation systems for hydrogen production, which should be additionally optimized to maximize the hydrogen yields. One effective method to determine the optimal C/N ratio is through the use of mathematical models. A relevant study was reported by Zhang *et al.*; they found that an optimal C/N ratio indeed enhanced the growth of photosynthetic microorganisms and improved their ability to produce biohydrogen. Subsequently, they adopted the response surface methodology and artificial neural networks integrated with genetic algorithms, revealing that the optimal C/N ratio reaching maximized hydrogen yields was contributed by the co-substrates. Thus, this C/N ratio optimization helped achieve more effective and efficient biohydrogen production processes.[41] In addition, supplementation of chemical nutrients can boost the fermentation efficiency by supporting bacterial growth and enzymatic activity. Vitamins, such as nicotinic acid and biotin, are crucial for maintaining bacterial health and enhancing hydrogen productivity in the fermentation system.[42] Phosphorus plays indispensable roles in synthesizing energy in the form of ATP, which fuels various metabolic processes in cells. Additionally, phosphorus also functions as a buffer, helping maintain pH balance in biochemical systems.[43]

By carefully monitoring and optimizing these process parameters, the hydrogen production efficiency through photo-fermentation can be significantly enhanced. Evidently, this improvement makes the process more viable as a method for renewable energy generation. In addition to energy production, photo-fermentation shows the distinct feature of sustainability, broadening the solutions to produce cleaner energy for the future.

2.4 Enhanced hydrogen production and mechanism

In the photo-fermentation process, PNSB absorb light energy to convert waste organics into CO_2 and H_2 *via* nitrogenase enzymes. However, challenges like low light conversion efficiency, compromised hydrogen production rates, and inhibition caused by toxic compounds can hinder the process.[44–46] For example, residual substrates and dark-colored wastewater reduce light penetration, while high ammonium concentrations suppress nitrogenase activity.[47] Despite facing such challenges, advanced technologies have been developed to improve the photo-fermentative efficiency towards biohydrogen production. Commonly adopted technologies to improve biohydrogen production are therefore comprehensively summarized and reviewed in the following sections.

2.4.1 Substrate pretreatment. Substrate pretreatment is essential to break down complex organic materials into simpler compounds that can be more readily utilized by microorganisms, and common pretreatment techniques include physical, chemical, and biological methods.[48] Specifically, physical pretreatments, such as milling or grinding, increase the surface area of the substrate, making it more accessible for microbial behaviors.[49,50] Chemical pretreatments, including acid or alkali treatments, help to solubilize complex polymers like cellulose and hemicellulose, leading to the release of fermentable sugars.[51] Biological pretreatments employ enzymes or microbial consortia to degrade lignocellulosic materials, converting them into simpler sugars without the need for harsh chemicals.[52] These pretreatment methods are designed to enhance the accessibility to more fermentable substrates, in turn improving the efficiency and hydrogen production performance. Notably, optimizing pretreatment conditions to deal with diverse biomass sources can largely increase the productivity and sustainability for biohydrogen generation, making it a crucial step in establishing effective photo-fermentation processes.

2.4.2 Genetic engineering. Biohydrogen production relies heavily on microbial metabolism; therefore, the development of highly performant strains is of crucial importance to improve hydrogen yield. Genetic engineering has become a key approach for enhancing bacterial performance under various environmental conditions, with strategies including the reduction of self-shading effects,[53] overexpression of nitrogenase genes,[54] enhancement of ATP content,[55] and improved ammonium tolerance.[56] When using photo-fermentative systems, however, most studies focus on using pure substrates (such as acetate, butyrate, or glucose) to boost the production of hydrogen,[53,54,57–59] with limited applications regarding the use of complex substrates like wastewater or biowaste. These pure substrates provide easily controlled environments but do not fully replicate the complex conditions of wastewater or biowaste. In a study, Wei *et al.* explored photo-assisted biological hydrogen production using a temperature-tolerant mutant of *Rhodobacter capsulatus* obtained through transposon mutagenesis.[60] They characterized and finally identified that the mutant strain exhibited improved hydrogen production capabilities at elevated temperatures, attributed to the mutant possessing the abilities to maintain photosynthetic activity and efficient electron transport under thermal stress. Therefore, this microbial metabolism adaptation methodology led to improved nitrogenase enzyme efficiency—a key factor in boost-

ing hydrogen production—highlighting that this strategy has promising potential for sustainable biohydrogen production under diverse and challenging environmental conditions. Inspired by this study, it is important to underscore that there is an urgent need to extend genetic engineering approaches to more complex and realistic substrates, such as those found in wastewater or biowaste, to maximize their practical applicability.

2.4.3 Immobilization technology. Immobilization technology represents an effective strategy to enhance the hydrogen production efficiency and productivity from biowaste, offering a pathway towards more sustainable and cost-effective biohydrogen production processes. This approach involves anchoring microbial cells onto support materials, which directly impacts the key mechanisms regarding hydrogen production. By immobilizing cells, the stability and concentration of the microbial community are significantly increased, creating a densely packed and metabolically active environment that optimizes substrate utilization and electron transfer for hydrogen generation.[61] A key advantage of immobilization lies in the enhanced resistance of microbial cells to environmental stresses, such as temperature fluctuations, pH variations, or the presence of inhibitory substances.[62] This increased resilience is essential for maintaining consistent hydrogen production under varying and potentially challenging industrial conditions. In addition, these stress-tolerant properties also play central roles in yielding consistent hydrogen in industrial applications where conditions may vary. Furthermore, immobilization reduces the risk of cell washout, a common issue in continuous fermentation processes, thereby ensuring a stable and prolonged production cycle.

Among the various immobilization techniques, biofilm-based systems are particularly noteworthy. Specifically, these systems enable microorganisms to form a biofilm—a thin, protective layer of cells—on the surface of the support material. The biofilm acts as a natural defense against cell washout, a common issue in continuous fermentation processes where cells may be lost to the effluent.[63] In these immobilized-cell systems, activated carbon fibers are especially effective carriers due to their large surface area.[64,65] Other materials with roughened surfaces, such as optical fibers,[66] porous glass plates,[67] and biomaterials using nanoparticles,[68] are also commonly utilized as carriers. These materials provide additional benefits such as enhanced light penetration or catalytic activity, which further intensify the metabolic processes to drive hydrogen production. Beyond the choice of carrier materials, operational parameters such as substrate concentration, light intensity, and flow rate also significantly influence the overall performance and long-term stability of immobilized-cell systems. For instance, an optimized light distribution within the bioreactor ensures the maximum activation of photosynthetic pathways, while the well-controlled flow rates prevent shear stress that might damage the biofilm.

Despite these advancements, the application of immobilization technology in large-scale reactors remains underexplored. Challenges such as maintaining biofilm integrity and balancing mass transfer in industrial settings require further investigations. Expanding research on large-scale immobilized reactors is essential to bridge the gaps between laboratory-scale studies and industrial applications, paving the way for efficient and sustainable biohydrogen production at scale.

2.4.4 Supplementary additives. In contrast to the aforementioned intensification tactics, the adoption of supplementary additives offers a simpler operational approach. This method primarily aims to enhance the hydrogen production process by introducing specific materials into the fermentation broth based on the metabolic requirements of the bacteria. The process can be optimized by adding: metal elements essential for bacterial growth or enzyme synthesis; photocatalytic nanomaterials that improve light absorption; and buffer solutions to mitigate acid inhibition. These additives effectively contribute to improving photo-fermentative hydrogen production.

Metal ions play pivotal roles in photo-fermentation systems, due to their functionality in bacterial metabolism and enzyme activation. Metal ions enhance photo-fermentative hydrogen production through multiple mechanisms (Fig. 3). As reported previously, Al-Mohammedawi *et al.* systemically investigated the impact of metal ions (specifically Fe and Mo) on photofermentative hydrogen production by using a mixture of pretreated brewery and restaurant effluents, where *Rhodobacter sphaeroides* was adopted.[69] Fe significantly boosted hydrogen yield (by 100%) by enhancing hydrogenase and ferredoxin activities in the electron transport chain. Mo, as a key component of nitrogenase, improved its efficiency in proton reduction under nitrogen-limited conditions. By optimizing Fe and Mo concentrations, the hydrogen production rate was notably enhanced, demonstrating their critical roles in the metabolic pathways of photo-fermentation. In addition to Fe and Mo, Eroglu *et al.* investigated the effects of Zn ions on the photo-fermentative hydrogen production performance, kinetics, and electronic distribution upon the use of HAU-M1.[70] The study achieved a 137% increase in hydrogen production, emphasizing the critical role of Zn ions. Zn significantly enhanced the hydrogen yield and rate by improving microbial activity and optimizing metabolic pathways. Kinetic analysis and electronic distribution studies revealed that Zn ions facilitated efficient electron transfer, strengthening the hydrogen evolution reaction. Subsequently, Xie *et al.* proved that Ca ions can enhance hydrogen production by promoting bioflocculation of photo-fermentative bacteria.[71] In detail, Ca ions facilitate the aggregation of bacterial cells, resulting in increased cell density and improved light absorption efficiency. This bioflocculation process optimized the metabolic activities of the bacteria, leading to a significant improvement in hydrogen production.

Beyond metal ions, nanomaterials have emerged as effective enhancers towards photo-fermentative hydrogen production, primarily attributed to the improved light absorption and electron transfer mechanisms (Fig. 3). For example, the integration of nanosized TiO_2, ZnO, SiC, and Fe_3O_4 with phototrophic bacteria such as *Rhodobacter sphaeroides* and

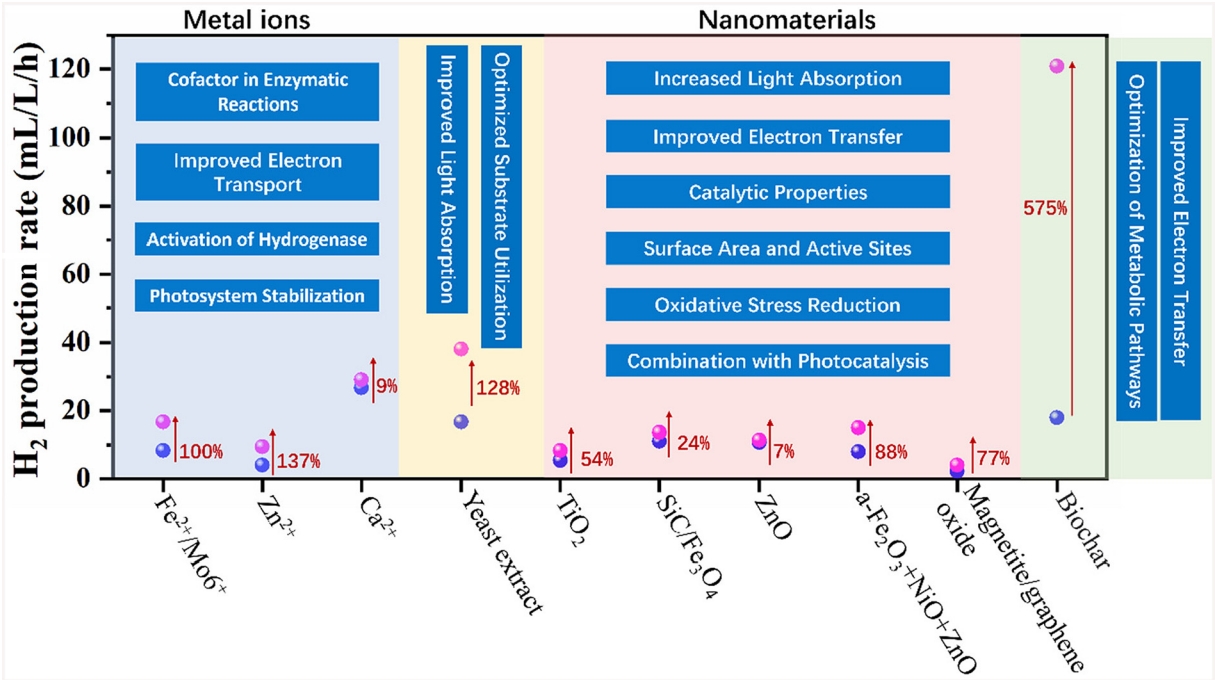

Fig. 3 The enhancing effects and mechanisms of supplementary additives on photo-fermentative hydrogen production from wastewater and biowaste.

Rhodopseudomonas has yielded promising results.[72–75] These nanoparticles act as photocatalysts, heightening light absorption and electron transfer processes, thereby increasing the hydrogen production efficiency under visible light irradiation, as supported by an enhancement of photo-fermentative production of hydrogen ranging from 24% to 88% (Fig. 3). Specifically, TiO_2 and ZnO nanoparticles enhance photo-fermentative activity by reducing the recombination rate of electron–hole pairs, allowing more electrons to participate in hydrogen production.[72,74,75] SiC and Fe_3O_4 nanoparticles further facilitate this process by providing additional active sites and increasing overall electron density.[73] The use of mixed bacterial cultures with Fe, Ni, and Zn-based nanoparticles has also demonstrated increased hydrogen production from industrial wastewater, indicating that these nanomaterials can serve as electron donors, thereby promoting microbial metabolism and hydrogenase activity. Additionally, Mostafa *et al.* showed that incorporating a magnetite/graphene oxide nanocomposite significantly enhanced hydrogen production from gelatinous wastewater.[76] This nanocomposite not only enabled the improvement of microbial growth and biofilm formation but also increased hydrogen production efficiency. Apart from the enhanced performance, the magnetite component provides magnetic properties that facilitate the separation and reuse of the catalyst, while graphene oxide enhances electron transfer processes and offers additional active sites for microbial interaction, leading to improved hydrogenase activity and overall hydrogen yield. These studies underscore the significant potential of nanomaterials in boosting the efficiency and scalability of biohydrogen production through photo-fermentation.

Beyond metal ions and nanomaterials, specific organic additives are also found to be effective in contributing to photo-fermentative hydrogen production. In the presence of *Rhodobium marinum*, Anam *et al.* demonstrated that the addition of yeast extract significantly enhances the photo-fermentative hydrogen production from bagasse and soy sauce wastewater.[77] Here, the yeast extract serves as a rich source of essential nutrients, vitamins, and growth factors, which stimulate the growth and metabolic activity of *Rhodobium marinum*. This, in turn, increases the efficiency of the hydrogenase enzyme and overall hydrogen production. Moreover, the yeast extract provides amino acids and peptides that can be utilized by the bacteria, further promoting biohydrogen production. However, Bu *et al.* found that biochar significantly enhances fermentative hydrogen production from sugarcane bagasse in a dark environment, boosting biohydrogen production by 371% and the maximum rate by 575%.[78] Biochar displays the features of selectively enriching and promoting the colonization of functional bacteria that are essential for realizing efficient hydrogen production. Additionally, biochar facilitates extracellular electron transfer, improving metabolic activity and electron flow within microbial communities. These combined effects lead to a notable increase in hydrogen yield, highlighting biochar's potential as a valuable additive in promoting biohydrogen production processes.

In light of the aforementioned discussion and understandings, each additive influences the metabolic and enzymatic

pathways of photo-fermentative bacteria. Metal ions act as essential cofactors, enhancing enzymatic reactions crucial for hydrogen production. Nanomaterials optimize light absorption and electron transfer, directly impacting hydrogen evolution efficiency. Organic additives enrich the microbial environment, promoting robust bacterial growth and metabolic activity. Collectively, these enhancements improve both the hydrogen production rate and yield, demonstrating their promising potential for scaled biohydrogen production systems.

2.4.5 Reactor design and condition optimization. Optimization of the reactor plays a pivotal role in enhancing photo-fermentative biohydrogen production by addressing critical factors such as light distribution, substrate availability, and microbial culture mixing.[48] An essential challenge in photo-fermentation is to ensure uniform light distribution, as uneven illumination impedes the photosynthetic efficiency of microorganisms. To address such issues, innovative designs such as flat-plate reactors,[79] tubular reactors,[80] and photobioreactors with internal light sources[81] have been developed, due to these designs being capable of improving light penetration, reducing shadowing effects, and optimizing photon capture, thereby increasing the overall hydrogen production rate. Furthermore, maximizing the surface area-to-volume ratio of reactors augments both light utilization and gas exchange, contributing to a higher hydrogen production efficiency.[82] The use of immobilized cell systems and biofilm reactors introduces additional advantages such as stabilized microbial communities and maintained high cell densities.[63] By providing a stable environment for microbial growth and maintaining high cell densities, these systems can enhance the overall productivity towards biohydrogen production.

In addition to reactor designing, integrating dark fermentation with photo-fermentation offers a synergistic approach for maximizing hydrogen production from biowaste.[83,84] This is because dark fermentation can produce hydrogen along with organic acids and alcohols, which can serve as substrates for subsequent photo-fermentation. This integration allows almost complete utilization of organic matter, enhancing both resource efficiency and hydrogen yield. There exist two commonly explored integration strategies: sequential and simultaneous systems. In sequential setups, the effluent from dark fermentation is fed into the photo-fermentation reactor, ensuring the continuous supply of substrates.[85] In contrast, simultaneous systems combine all relevant processes within a single reactor, enabling efficient substrate conversion in a co-culture environment. Therefore, the optimization of operational parameters of these integrated systems (such as pH, temperature, and substrate concentration) can align the metabolic requirements from both dark- and photo-fermentative microorganisms. Sophisticatedly designed reactors that support the co-culture of diverse microbial communities are synergic, leading to higher hydrogen yields and improved process stability.

Overall, the integrated approach of innovative reactor design and process integration represents a powerful strategy to enhance the efficiency, scalability, and sustainability of biohydrogen produced from photo-fermentative systems. It is important to address these complex processes occurring in photo-fermentative systems from physical and biological aspects, which can pave the way for more effective utilization of renewable resources to generate hydrogen.

3. Biomethane production through photo-fermentation

3.1 The process of photo-fermentative biomethane production and mechanisms

Methane production from photo-fermentation systems involves the indirect utilization of light energy to facilitate the anaerobic degradation of organic matter, leading to methane generation. Unlike direct hydrogen production, methane production from photo-fermentation relies on a multi-step process where light conditions enhance the activity of microbial communities under anaerobic conditions.[86] The process begins with the introduction of wastewater containing organic substrates into a bioreactor. Photosynthetic bacteria, primarily PNSB, absorb light energy to catalytically trigger the breakdown of complex organic molecules into simpler compounds. These bacteria, along with other anaerobic microorganisms, create a synergistic environment where organic matter is progressively degraded through multiple stages of hydrolysis, acidogenesis, acetogenesis, and finally methanogenesis. In methanogenesis, methanogenic archaea convert intermediate products such as acetate, hydrogen, and carbon dioxide into methane.[87] The methane production efficiency is significantly influenced by light conditions, which enhance the metabolic activity of photosynthetic bacteria and, in turn, improve the overall anaerobic degradation process.[14] In summary, photo-fermentation produced methane is an indirect, multi-step process that can be enhanced through targeted optimization of microbial activity and environmental conditions, leveraging light energy to improve the efficiency of anaerobic degradation and methane generation (Fig. 4).

When processing wastewater or biowaste for producing photo-fermentative methane, the optimization of light intensity and duration is crucial, as improper lighting can significantly reduce methane yield. As previously evidenced, Toya *et al.* conducted a study to examine the effects of photo-irradiation on the anaerobic digestion of waste sewage sludge, with a focus on methane and hydrogen sulfide production.[88] The results revealed that photo-irradiation reduced methane production, likely due to the inhibition of methanogenic activity. Yang *et al.* investigated the optimization of illumination time in a carbon felt fluidized bed bioreactor to enhance methane production during thermophilic anaerobic digestion.[89] Their findings demonstrated that the proper adjustment of illumination time plays a pivotal role in enhancing methane production by directly impacting microbial activity and overall process efficiency. These studies underscore the critical importance of precise light management in maximizing biogas production, particularly under thermophilic con-

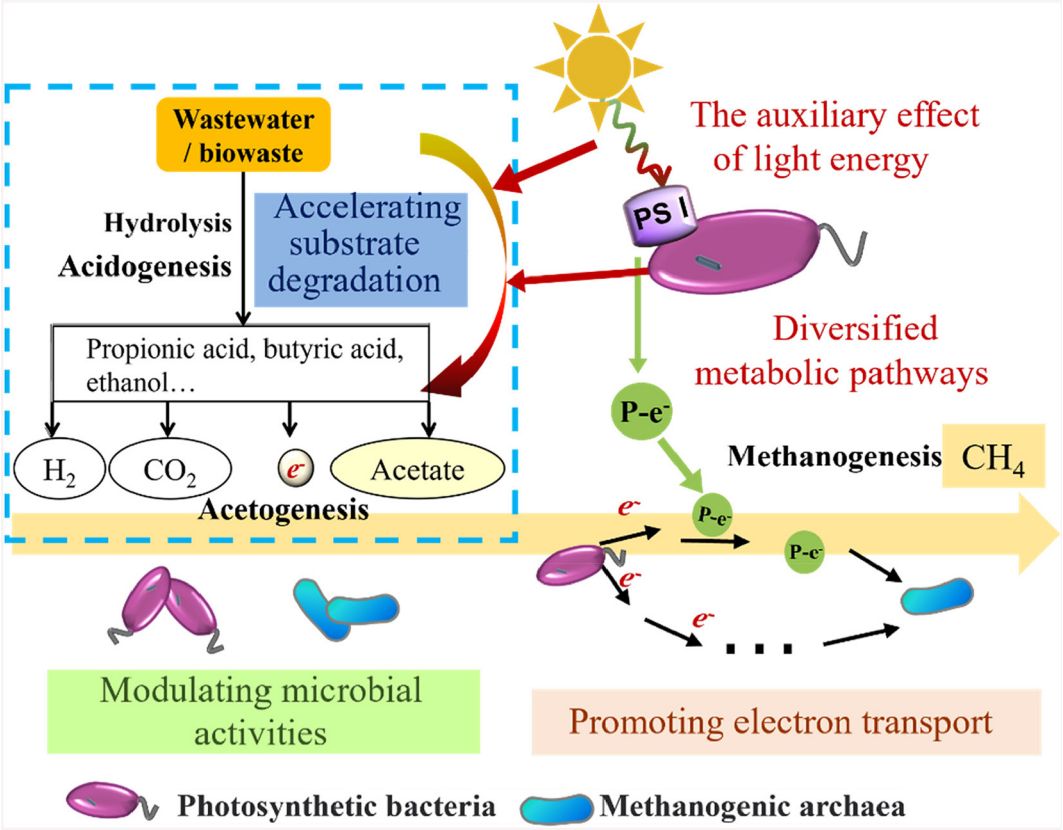

Fig. 4 Mechanism diagram of photo-fermentative biomethane production.

ditions, where microbial dynamics is more sensitive to environmental factors. By alternating conditions such as light intensity, pH, and temperature, the efficiency of methane production through photo-fermentation can be significantly boosted, making it a promising technology for sustainable bioenergy generation.

The integration of photo-fermentation and methanogenesis can occur within a single reactor or through sequential reactors. In a single-reactor setup, phototrophic bacteria and methanogens coexist and interact directly, facilitating efficient substrate conversion and methane production. In a sequential system, the effluent from the photo-fermentation stage, rich in organic acids and alcohols, is transferred to a methanogenic reactor, where methane production is completed. This integrated approach not only boosts the overall energy yield from organic waste but also reduces greenhouse gas emissions by converting carbon-rich substrates into valuable biofuels. For example, Xia *et al.* explored the sequential production of hydrogen and methane from glutamic acid using a combined photo-fermentation process that involved methanogenesis. Initially, photosynthetic bacteria convert glutamic acid into hydrogen, while the remaining organic residues are subsequently utilized by methanogenic archaea to produce methane. This method benefits energy recovery from a single substrate, highlighting the potential for efficient bioenergy production.[90] Furthermore, the advantages of a three-stage fermentation process, combining dark hydrogen, photo-hydrogen, and methane fermentation, have been emphasized for enhanced energy recovery from various waste streams.[91,92] This approach leverages different microbial consortia at each stage, efficiently converting complex organic materials into biohydrogen and biomethane. Additionally, integrating ammonium removal or utilizing specific conditions, such as high CO_2 and sodium stress, further enhances the process efficiency, making it a highly effective strategy to maximize bioenergy output while treating wastewater and biowaste.

Relevant studies related to biomethane production from wastewater and biowaste through photo-fermentation are shown in Table 2. These studies verify the great potential of photo-fermentation in enhancing methane yields compared to conventional dark fermentation. As supported by the detailed values in Table 2, methane production through photo-fermentation has increased by 75.2%, 470%, 70.4%, and 189.7% compared to dark fermentation under various conditions, reflecting the transformative impact of light on the anaerobic digestion process.[93–96] Neshat *et al.* observed that optimized illumination intensity significantly improved the methane content in biogas when fermenting cattle manure leachate, with the methane concentration increasing from 20% under dark conditions to 80% in hybrid bioreactors under illuminated conditions.[97] This increase can be attributed to the stimulation of photosynthetic bacteria (such as PNSB), which thrive under

Table 2 Overview of studies related to biomethane production from wastewater and biowaste through photo-fermentation

Feedstock	Inoculum	CH_4 yield (dark)	CH_4 yield (photo)	CH_4 yield (enhanced)	Ref.
Sodium acetate + glucose	Anaerobically digested sludge	113 mL g^{-1} DOCremoval	198 mL g^{-1} DOCremoval	—	93
Cattle manure leachate	PNSB	About 0.01 L CH_4 per g CODremoved	0.057 L CH_4 per g CODremoved	—	94
Cattle manure leachate	Anaerobically digested sludge	20% CH_4 content	80%	—	97
Municipal sludge	Anaerobically digested sludge	179.2 mL CH_4 per g COD	305.4 mL CH_4 per g COD	—	95
Sodium acetate + glucose	Anaerobically digested sludge	9.7 mL CH_4 per d reactor	28.1 mL CH_4 per d reactor	—	96
Terephthalic acid wastewater	Anaerobically digested sludge	1.814 mmol L^{-1} d^{-1}	2.218 mmol L^{-1} d^{-1}	2.968 mmol L^{-1} d^{-1}	14
Glucose + humic acid	Anaerobically digested sludge	About 100 mL g^{-1} VS	223.0 mL g^{-1} VS	293.7 mL g^{-1} VS	98

light conditions. Therefore, these illumination-stimulated microorganisms will strengthen the metabolic pathways in the system, enabling more efficient substrate utilization and methanogenesis.

The studies exemplified in Table 2 also demonstrate that the effect of light extends beyond methane yield to influence the overall efficiency of anaerobic digestion. For instance, light conditions facilitate photosynthetic bacteria to degrade complex organic substrates, which convert these substrates into simpler compounds that are more readily available for the following methanogenic archaea. This cooperative interaction between photosynthetic and methanogenic microorganisms ensures a higher conversion efficiency of organic matter to methane. Additionally, light exposure has been shown to impact microbial community compositions and electron transport mechanisms within anaerobic systems. For example, Qian *et al.* have provided evidence that illumination promotes a shift in microbial populations toward more efficient methanogens, such as *Methanosarcina* species, and enhances electron transfer processes critical for methanogenesis.[95] This dual effect contributed by microbial selection and improved electron transport considerably boosts methane production. Notably, the integration of light into anaerobic digestion processes can also lead to operational benefits, as demonstrated by Tada *et al.*, who have confirmed that light-assisted anaerobic digestion not only enhances biogas yield but also accelerates the degradation of refractory organic compounds, such as humic acids that are challenging to be degraded.[96] This discovery indicates that photo-fermentation is also particularly effective to cope with complex biowaste streams. In addition, our previous study found that light conditions can accelerate substrate degradation because photosynthetic bacteria are able to use light energy to convert organic matter into simpler compounds.[14] Moreover, light energy has an auxiliary effect on substrate degradation, as the involvement of photosynthetic microorganisms diversifies the metabolic pathways within the system, further promoting substrate degradation.

Collectively, the findings presented in Table 2 and specifically discussed studies underscore the critical roles of light in modulating microbial activities, accelerating substrate degradation rates, and promoting electron transport processes (Fig. 4). By leveraging such instrumental synergistic effects in photo-fermentation systems, anaerobic digestion systems can achieve enhanced methane production, reduced residual organic matter, and greater process efficiency. Based on the insightful understandings of these exemplified advancements, the great potential of adopting photo-fermentation technology as a sustainable and innovative approach for optimizing biomethane production from widely available wastewater and biowaste is recognized.

The impact of feedstock type, inoculum composition, and enhanced technologies on biomethane production efficiency through photo-fermentation is evident across various studies. For instance, substrates such as sodium acetate, glucose, cattle manure leachate, municipal sludge, and humic acid demonstrate varying degrees of methane production capacity under light-assisted conditions. Advanced photocatalysts, including g-C_3N_4 and NCQDs, have been shown to significantly enhance light utilization efficiency and microbial activity, driving higher methane production performance. These photocatalysts improve light absorption, facilitate electron transfer, and promote microbial interactions critical for methanogenesis. When compared with different studies, it is concluded that the complexity of feedstocks and the characteristics of microbial communities are key determinants in dictating the eventual methane yield. Enhanced technologies such as the proper utilization of light intensity, microbial population shift, and electron transfer mechanism enable the amplification of photo-fermentation effects, in turn determining biofuel production efficiency. By linking these findings, this review provides a holistic framework to understand how different parameters co-influence biomethane production, elaborating on the recent progress and still existing challenges in exploring photo-fermentative bioenergy systems.

3.2 Enhanced photo-methanogenesis and mechanisms

The process of photo-methanogenesis can be further enhanced through certain methods; however, this area is currently underexplored. Our reported study found that the incorporation of g-C_3N_4 significantly increased methane production during the photo-fermentation process.[14] In the system, g-C_3N_4 acts as an efficient photocatalyst, providing a unique mechanism that boosts the overall photo-fermentation process. Firstly, g-C_3N_4 possesses excellent light absorption properties and a suitable bandgap, which allows it to harness visible light effectively. Upon illumination, g-C_3N_4 generates

electron–hole pairs, where the photogenerated electrons play a crucial role in reducing protons to produce hydrogen. This hydrogen subsequently serves as an electron donor for methanogenic archaea, thereby enhancing methane production. Moreover, its high surface area provides more active sites for microbial attachment and interaction, promoting microbial activity and stability. Additionally, the presence of g-C_3N_4 helps mitigate electron recombination, thus improving the efficiency of electron transfer processes.

Liu *et al.* investigated the role of N-doped carbon quantum dots (NCQDs) in enhancing the photo-anaerobic digestion efficiency for methane production, specifically focusing on the breakdown of humic acid.[98] NCQDs, with their unique electronic properties that generate reactive oxygen species (ROS) under visible light, act as effective photocatalysts in anaerobic digestion systems, significantly boosting the degradation of complex humic substances and increasing the availability of simpler substrates for methanogenic archaea. Firstly, NCQDs improve light absorption and utilization efficiency, extending the absorption spectrum into the visible range and thereby maximizing the photonic energy harnessed for catalytic reactions. Secondly, the high surface area and abundant active sites of NCQDs facilitate the adsorption and interaction of humic acid molecules, promoting their oxidative breakdown. The ROS generated by NCQDs under light exposure attack the aromatic structures of humic acids, leading to their fragmentation into smaller, more biodegradable molecules. Furthermore, NCQDs exhibit excellent electron-donating properties, which help in maintaining a favorable redox environment for methanogenesis. By efficiently transferring photogenerated electrons to methanogenic microbes, NCQDs reduce the potential energy barriers for bioconversion processes. This electron transfer capability not only accelerates the reduction reactions essential for methane production but also mitigates the inhibitory effects of intermediate compounds such as volatile fatty acids.

Currently, as aforementioned, there are only two studies on enhancing photo-methanogenesis; however, photo-methanogenesis can be further improved in various ways. These include optimizing light intensity and wavelength to match the absorption spectrum of photosynthetic bacteria, maintaining optimal environmental conditions (such as pH and temperature), genetic engineering of microbial strains, and using co-cultured bacteria and archaea for metabolic interaction enhancements. These enhancement strategies need to be comprehensively explored by scientists to advance photo-fermentation systems for clean energy generation.

4. Comparison of hydrogen and methane production through photo-fermentation

Photo-fermentation for biohydrogen production and photo-fermentation for biomethane production are two distinct bioenergy conversion processes, each showing unique principles, feedstock utilization, environmental impacts, efficiencies, and yields.

Firstly, the fundamental principles of these processes differ significantly. Photo-fermentation for hydrogen production leverages the capabilities of photosynthetic bacteria, such as PNSB, which utilize light energy to drive the photolysis of organic substrates, generating hydrogen gas as a byproduct. This process is inherently anaerobic and relies on the photosynthetic electron transport chain to split water molecules or organic acids, leading to the production of hydrogen.[8] In contrast, photo-fermentation for methane production involves the use of light to enhance the activities of anaerobic microorganisms, including photosynthetic bacteria and archaea, within the anaerobic digestion process. Here, light primarily serves to stimulate the growth and metabolic activities of these microorganisms, indirectly enhancing methane production through the fermentation and subsequent methanogenesis of organic substrates.[14] The role of light in methane production is more about optimizing microbial ecosystems and electron transfer processes rather than directly generating methane.

To gain a better understanding regarding the production of biohydrogen and biomethane, distinct differences in productivity, efficiency, and operational conditions are introduced in the following contexts. Photo-fermentation processes typically achieve higher hydrogen yields under optimal light conditions, leveraging substrates like organic acids with efficiencies ranging between 20 and 30% under controlled environments. As for CH_4 production, it benefits from microbial consortia that allow near-complete substrate utilization under mesophilic (35–40 °C) or thermophilic (50–55 °C) conditions. Integrating these two distinct processes, such as using VFAs generated during methanogenesis to feed photo-fermentation, may offer a solution to maximize resource recovery and improve overall bioenergy yields, also underscoring the complementary nature of these bioenergy systems. These differences highlight the need for process optimization tailored to the feedstock and energy demand scenarios.

Beyond detailed summary and mechanism elucidation, this review also compares and evaluates biohydrogen and biomethane production based on the reported study by Liu *et al.*[99] and experimental data, focusing on yield, efficiency, and economic and environmental impacts (Fig. 5). The experimental data analyzed in this study were obtained using corn straw as the substrate with a solid content of 15%. Compared to anaerobic digestion, the photo-fermentation process demonstrated a 9.2% increase in methane yield, a 30.5% reduction in the production cycle, and a 20.6% enhancement in methane content. Production yield is a key indicator of the substrate conversion efficiency, representing the amount of substrate converted into the target product per unit mass.[100] The hydrogen production yield is significantly lower, possibly due to the limited substrate utilization efficiency during photo-fermentation and dark-fermentation or the constraints of microbial metabolism in hydrogen generation. In contrast, methane demonstrates a largely improved production capacity, making it the preferred choice for energy development focused on high yields (Fig. 5).

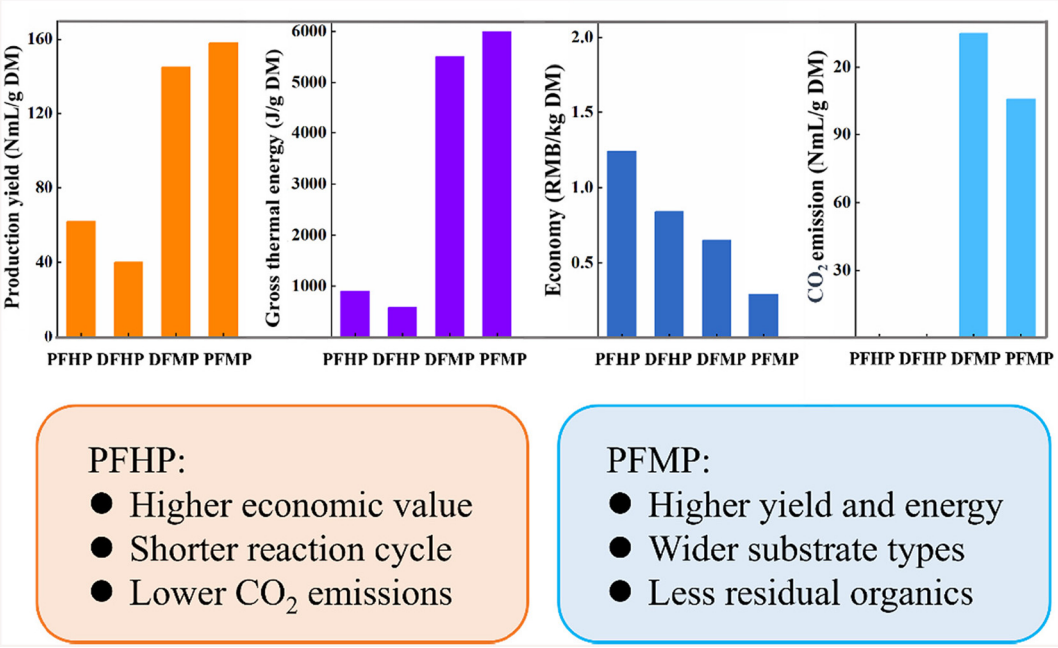

Fig. 5 Comprehensive analysis of biohydrogen and biomethane produced from photo-fermentation systems. PFHP represents photo-fermentative hydrogen production. DFHP represents dark-fermentative hydrogen production. DFMP represents photo-fermentative methane production. PFMP represents photo-fermentative methane production.

The economic assessment of target products generated from photo-fermentation processes serves as a vital metric to evaluate its progress towards industrial-scale production.[101] Due to advantages such as higher hydrogen yield, excellent utilization of light energy, and reduced substrate requirements, photo-fermentation hydrogen production has lower economic costs compared to dark fermentation (Fig. 5)[102] The economic evaluation of hydrogen and methane produced from photo-fermentation systems reveals distinct differences according to their technical characteristics and market potential. Hydrogen produced from photo-fermentation offers higher economic value due to its role as a clean energy source with extensive applications in industries, transportation and chemicals. Biohydrogen has a higher market price, approximately 0.02 RMB per L H_2, compared to 2.25 RMB per m^3 of CH_4.[99] However, this process demands high-quality feedstocks such as sugars and volatile fatty acids, alongside advanced photobioreactor designs, which increase the initial investment costs. Despite these challenges, the shorter production cycle and the accessibility to utilize by-products like acetic acid enhance the overall economic feasibility of hydrogen production.

In contrast, photo-fermentation for methane production is less efficient and economically attractive due to its lower market value and the slower growth rate of methanogenic bacteria, which require longer processing times and lower redox potential for metabolism. The cost-effectiveness of biomethane production lies in its ability to process diverse organic waste streams with fewer stringent requirements, leading to lower operational expenses. Additionally, methane's higher energy density and storage efficiency provide long-term cost advantages, making it suitable for waste management applications. Government carbon credits aiming for renewable energy projects may also improve the economic feasibility of methane production in certain regions. Overall, hydrogen production offers faster returns on investment and higher market potential, especially in regions prioritizing renewable energy. However, methane production is better suited for large-scale, stable operation utilizing organic waste, providing environmental and economic benefits in waste management.

The target hydrogen produced from photo-fermentation does not result in greenhouse gas emissions, whereas biomethane production is associated with higher greenhouse gas emissions.[99] The higher CO_2 emissions in biomethane production can be attributed to the more complex metabolic pathways involved in methane generation. Optimizing photo-fermentative methane production with carbon capture technologies could mitigate its environmental impact while maintaining its high yield. Therefore, finding effective ways to utilize CO_2 generated during biomethane production is crucial for reducing greenhouse gas emissions. Notably, as profiled in Fig. 5, biomethane demonstrated higher energy yield and greater thermal energy than biohydrogen. Once biomethane is produced, it is capable of accumulating massive amounts of high energy density gas over long-term operation. On top of that, methane production processes typically result in lower environmental impacts, attributed to their ability of effectively handling diverse and high-load organic waste streams.

Photo-fermentation systems for producing hydrogen and methane leverage the synergy of light and microorganisms to convert organic substrates into valuable biofuels, although

they operate on distinct principles with unique advantages and challenges. Hydrogen produced *via* photo-fermentation stands out because of its potential to reduce CO_2 emissions and its economic benefits, although it requires specific substrates and harsh conditions. Conversely, methane generated from photo-fermentation offers greater versatility and efficiency in substrate utilization and energy recovery, making it more practical for large-scale waste management and renewable energy generation. Together, these photo-fermentative processes align well with the principles of green chemistry, including resource recovery, waste valorization, and renewable energy production, demonstrating significant prospects for attaining environmental sustainability while consuming and purifying low-value waste. By integrating these principles, photo-fermentation will represent a promising technology to produce cleaner and more sustainable energy from waste and minimize the environmental impacts during bioenergy production processes.

5. Conclusions and outlook

This review highlights the potential of exploring photo-fermentation technology to produce biohydrogen and biomethane from wastewater and biowaste, emphasizing their processes, mechanisms and sustainability benefits. Biohydrogen production offers marked light-utilization efficiency and rapid substrate conversion by virtue of photosynthetic bacteria, while biomethane production relies on synergistic interactions between photosynthetic bacteria and methanogenic archaea, providing stable and continuous energy output. The bioenergy production processes combine renewable energy generation with waste treatment, aligning with global sustainability goals. Despite their advantages and progress, the practical adoption of such technologies faces challenges related to scalability, cost, and operational stability. To bridge the gap between research and industrial application, we propose the following strategies:

(i) Future research should focus on improving light distribution systems tailored to the absorption spectra of photosynthetic bacteria, optimizing photobioreactor design to enhance light penetration, and developing new materials or technologies to achieve more uniform light distribution across the entire culture. Additionally, efforts should be directed towards engineering microbial strains with enhanced productivity and environmental resilience. Integrating photo-fermentation with other biotechnologies, such as nutrient recovery systems, could further improve overall efficiency. The realization of these measures can optimize the resource utilization efficiency and make bioenergy production more sustainable.

(ii) The improvement of methane production requires fine-tuned operation parameters such as light intensity, pH, and temperature, as these operation parameters enable the enhancement of microbial activity. Co-culturing photosynthetic bacteria with methanogenic archaea, applying genetic engineering, and exploring photocatalytic materials can further boost substrate degradation as well as bioenergy formation yield.

(iii) Retrofitting existing mature anaerobic digesters with energy-efficient LED lighting systems is a low-carbon strategy to conduct photo-fermentation, which does not require significant infrastructure changes, costs and land use. Additionally, hybrid photobioreactors with advanced light-capturing materials and modular designs can enhance scalability and allow the treatment of diverse waste streams efficiently.

(iv) The selective production of biohydrogen or biomethane depends on wastewater compositions and energy demands. Hydrogen is ideal for clean energy-associated applications and requires easily degradable substrates. While the production of methane can use complex substrates, the produced methane can be used in existing biogas infrastructure for heating and power generation.

Photo-fermentation technology holds transformative potential for the realization of dual benefits: renewable energy generation and sustainable waste treatment. By addressing current challenges through innovative microbial engineering, reactor designing and process integration, photo-fermentation technology will contribute significantly to the challenging areas of resource recovery and clean energy transition. As expected, the wide adoption of photo-fermentation technology will pave the way for achieving a sustainable and circular bioeconomy.

Author contributions

Dandan Xie: conceptualization, collecting data, and writing – original draft. Lingfen Kong: investigation and formal analysis. Jiehua Hu: discussion and data interpretation. Heng Li and Yuanpeng Wang: funding acquisition, writing – review and editing, and supervision. All authors read and approved the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (U24A20543, 22038012, and 22108231), the Natural Scientific Foundation of Fujian Province (2022J01391), the Natural Science Foundation of Xiamen (3502Z202372094), and the Natural Scientific Project of Xiamen Ocean Vocational College (KYZ202208).

References

1 M. A. H. Khataybeh and A. Akgüç, *The Role of Design, Construction, and Real Estate in Advancing the Sustainable Development Goals*, 2023, vol. 151.

2 M. Mitra, N. R. Singha and P. K. Chattopadhyay, *Sustain. Energy Technol. Assessments*, 2023, **57**, 103295.
3 M. R. Hasan, N. Anzar, P. Sharma, S. J. Malode, N. P. Shetti, J. Narang and R. R. Kakarla, *Bioresour. Technol. Rep.*, 2023, **23**, 101542.
4 S. Y. Lee, R. Sankaran, K. W. Chew, C. H. Tan, R. Krishnamoorthy, D.-T. Chu and P.-L. Show, *BMC Energy*, 2019, **1**, 4.
5 H. C. Ong, W.-H. Chen, A. Farooq, Y. Y. Gan, K. T. Lee and V. Ashokkumar, *Renewable Sustainable Energy Rev.*, 2019, **113**, 109266.
6 V. G. Gude, *Clean Technol. Environ. Policy*, 2018, **20**, 911–924.
7 C. Hitam and A. A. Jalil, *Biomass Convers. Biorefin.*, 2023, **13**, 8465–8483.
8 F. Nadeem, H. Zhang, N. Tahir, Z. Zhang, R. Rani Singhania, M. Shahzaib, H. Ramzan, M. Usman, M. Ur Rahman and Q. Zhang, *Bioresour. Technol.*, 2023, **382**, 129221.
9 B. Senthil Rathi, P. Senthil Kumar, G. Rangasamy and S. Rajendran, *Int. J. Hydrogen Energy*, 2024, **52**, 115–138.
10 S. Bosu and N. Rajamohan, *Int. J. Hydrogen Energy*, 2024, **52**, 61–79.
11 C. Putatunda, M. Behl, P. Solanki, S. Sharma, S. K. Bhatia, A. Walia and R. K. Bhatia, *Int. J. Hydrogen Energy*, 2023, **48**, 21088–21109.
12 V. S. Muthuraman and N. Kasianantham, *Process Saf. Environ. Prot.*, 2023, **174**, 694–721.
13 J. Zeng, H. Zeng and Z. Wang, *Int. J. Energy Res.*, 2022, **46**, 10301–10319.
14 H. Li, L. F. Ye, Y. X. Li, L. Zhou, D. Xia and Y. P. Wang, *Renewable Energy*, 2024, **221**, 119852.
15 B. Hu, Y. M. Li, S. N. Zhu, H. R. Zhang, Y. Y. Jing, D. P. Jiang, C. He and Z. P. Zhang, *Bioresour. Technol.*, 2020, **305**, 122900.
16 M. Yetis, U. Gündüz, I. Eroglu, M. Yücel and L. Türker, *Enzyme Microb. Technol.*, 2000, **25**, 1035–1041.
17 T. Assawamongkholsiri, A. Reungsang, P. Plangkang and S. Sittijunda, *Int. J. Hydrogen Energy*, 2018, **43**, 3605–3617.
18 K. Seifert, M. Waligorska and M. Laniecki, *Int. J. Hydrogen Energy*, 2010, **35**, 4085–4091.
19 K. Anam, M. S. Habibi, T. U. Harwati and D. Susilaningsih, *Int. J. Hydrogen Energy*, 2012, **37**, 15436–15442.
20 G. H. Zheng, L. Wang and Z. H. Kang, *Renewable Energy*, 2010, **35**, 2910–2913.
21 K. Seifert, M. Waligorska and M. Laniecki, *Int. J. Hydrogen Energy*, 2010, **35**, 9624–9629.
22 C. Pintucci, A. Giovannelli, M. L. Traversi, A. Ena, G. Padovani and P. Carlozzi, *Renewable Energy*, 2013, **51**, 358–363.
23 H. Znad, H. Al-Mohammedawi and M. R. Awual, *Biomass Bioenergy*, 2021, **144**, 105899.
24 Y. A. Purwanto, R. P. A. Setiawan and B. Susilo, *Int. J. Hydrogen Energy*, 2024, **56**, 323–329.
25 J. X. W. Hay, T. Y. Wu, J. C. Juan and J. M. Jahim, *Environ. Sci. Pollut. Res.*, 2017, **24**, 10354–10363.
26 P. M. Budiman and T. Y. Wu, *Energy Convers. Manage.*, 2016, **119**, 142–150.
27 A. Adessi, M. Venturi, F. Candeliere, V. Galli, L. Granchi and R. De Philippis, *Int. J. Hydrogen Energy*, 2018, **43**, 9569–9576.
28 A. Adessi, J. B. McKinlay, C. S. Harwood and R. De Philippis, *Int. J. Hydrogen Energy*, 2012, **37**, 15893–15900.
29 S. R. Das and N. Basak, *Biomass Convers. Biorefin.*, 2024, **14**, 4791–4811.
30 T. Zhang, D. P. Jiang, H. Zhang, Y. Y. Jing, N. Tahir, Y. Zhang and Q. G. Zhang, *Int. J. Hydrogen Energy*, 2020, **45**, 3807–3814.
31 Z. P. Zhang, H. R. Zhang, Y. M. Li, C. Y. Lu, S. N. Zhu, C. He, F. Ai and Q. G. Zhang, *Bioresour. Technol.*, 2020, **312**, 123570.
32 T. Zhang, D. Jiang, H. Zhang, Y. Jing, N. Tahir, Y. Zhang and Q. Zhang, *Int. J. Hydrogen Energy*, 2020, **45**, 3807–3814.
33 S. Y. Guo, C. Y. Lu, K. X. Wang, J. Wang, Z. P. Zhang, Y. Y. Jing and Q. G. Zhang, *Bioengineered*, 2020, **11**, 291–300.
34 Q. Zhou, P. Zhang and G. Zhang, *Bioresour. Technol.*, 2014, **171**, 330–335.
35 B. Uyar, I. Eroglu, M. Yücel, U. Gündüz and L. Türker, *Int. J. Hydrogen Energy*, 2007, **32**, 4670–4677.
36 K. Bolatkhan, B. D. Kossalbayev, B. K. Zayadan, T. Tomo, T. N. Veziroglu and S. I. Allakhverdiev, *Int. J. Hydrogen Energy*, 2019, **44**, 5799–5811.
37 M. F. Tiang, M. A. F. Hanipa, P. M. Abdul, J. M. Jahim, S. S. Mahmod, M. S. Takriff, C.-H. Lay, A. Reungsang and S.-Y. Wu, *Int. J. Hydrogen Energy*, 2020, **45**, 13211–13230.
38 A. Patel, L. Matsakas, U. Rova and P. Christakopoulos, *Bioresour. Technol.*, 2019, **278**, 424–434.
39 G. Melitos, X. Voulkopoulos and A. Zabaniotou, *Renewable Energy Environ. Sustainability*, 2021, **6**, 45.
40 S. Guo, C. Lu, K. Wang, J. Wang, Z. Zhang, Y. Jing and Q. Zhang, *Bioengineered*, 2020, **11**, 291–300.
41 X. Zhang, Q. Zhang, Y. Li and H. Zhang, *Bioresour. Technol.*, 2023, **374**, 128789.
42 P. M. Budiman and T. Y. Wu, *Energy Convers. Manage.*, 2018, **165**, 509–527.
43 S. Mona, S. S. Kumar, V. Kumar, K. Parveen, N. Saini, B. Deepak and A. Pugazhendhi, *Sci. Total Environ.*, 2020, **728**, 138481.
44 A. M. Abdalla, S. Hossain, O. B. Nisfindy, A. T. Azad, M. Dawood and A. K. Azad, *Energy Convers. Manage.*, 2018, **165**, 602–627.
45 H. Song, S. Luo, H. Huang, B. Deng and J. Ye, *ACS Energy Lett.*, 2022, **7**, 1043–1065.
46 D. Cheng, H. H. Ngo, W. Guo, S. W. Chang, D. D. Nguyen, X. T. Bui, W. Wei, B. Ni, S. Varjani and N. B. Hoang, *Bioresour. Technol.*, 2022, **357**, 127341.
47 A. Adessi, *Hydrogen production using Purple Non-Sulfur Bacteria (PNSB) cultivated under natural or artificial light conditions with synthetic or fermentation derived substrates*, Firenze University Press, 2013.

48 Q. Zhang, S. Zhu, Z. Zhang, H. Zhang and C. Xia, *Bioresour. Technol.*, 2021, **340**, 125601.
49 Z. Zhang, N. Tahir, Y. Li, T. Zhang, S. Zhu and Q. Zhang, *Renewable Energy*, 2019, **141**, 298–304.
50 W. Yi, F. Nadeem, G. Xu, Q. Zhang, N. Joshee and N. Tahir, *J. Cleaner Prod.*, 2020, **269**, 122386.
51 T. Zhang, D. Jiang, H. Zhang, D.-J. Lee, Z. Zhang, Q. Zhang, Y. Jing, Y. Zhang and C. Xia, *Bioresour. Technol.*, 2020, **304**, 122999.
52 Y. Zhang, H. Zhang, D.-J. Lee, T. Zhang, D. Jiang, Z. Zhang and Q. Zhang, *Bioresour. Technol.*, 2020, **305**, 123062.
53 Y. Zhang, H. Yang and L. Guo, *Int. J. Hydrogen Energy*, 2016, **41**, 190–197.
54 H. Ma, H. Yang, X. Zheng, T. Lie and W. Yan, *Int. J. Hydrogen Energy*, 2021, **46**, 3742–3752.
55 Y. Zhang, J. Hu, H. Ma, H. Yang and L. Guo, *Int. J. Hydrogen Energy*, 2017, **42**, 9641–9649.
56 X.-M. Wu, L.-Y. Zhu, L.-Y. Zhu and L. Wu, *Int. J. Hydrogen Energy*, 2016, **41**, 22824–22830.
57 X. Zheng, H. Ma, J. Zhang, W. Yan and H. Yang, *Int. J. Hydrogen Energy*, 2019, **44**, 15823–15832.
58 C. Ma, X. Wang, L. Guo, X. Wu and H. Yang, *Bioresour. Technol.*, 2012, **118**, 490–495.
59 Q. Fu, Y. Li, N. Zhong, Q. Liao, Y. Huang, A. Xia, X. Zhu and Y. Hou, *Int. J. Hydrogen Energy*, 2017, **42**, 27523–27531.
60 X. Wei, J. Feng, W. Cao, Q. Li and L. Guo, *Bioresour. Technol.*, 2021, **320**, 124286.
61 A. A. Najim, A. Y. Radeef, I. Al-Doori and Z. H. Jabbar, *J. Chem. Technol. Biotechnol.*, 2024, **8**, 1707–1733.
62 I. Moreno-Garrido, *Bioresour. Technol.*, 2008, **99**, 3949–3964.
63 E. Sagir and S. Alipour, *Renewable Sustainable Energy Rev.*, 2021, **141**, 110796.
64 G.-J. Xie, B.-F. Liu, J. Ding, D.-F. Xing, H.-Y. Ren, W.-Q. Guo and N.-Q. Ren, *Biomass Bioenergy*, 2012, **44**, 122–129.
65 L. Wang, F. Jia, D. Wu, Q. Wei, Y. Liang, Y. Hu, R. Li, G. Yu, Q. Yuan and J. Wang, *Appl. Surf. Sci.*, 2020, **527**, 146793.
66 C.-L. Guo, X. Zhu, Q. Liao, Y.-Z. Wang, R. Chen and D.-J. Lee, *Bioresour. Technol.*, 2011, **102**, 8507–8513.
67 R. Zagrodnik, K. Seifert, M. Stodolny and M. Laniecki, *Int. J. Hydrogen Energy*, 2015, **40**, 5062–5073.
68 Y. Li, N. Zhong, Q. Liao, Q. Fu, Y. Huang, X. Zhu and Q. Li, *Int. J. Hydrogen Energy*, 2017, **42**, 5793–5803.
69 H. H. Al-Mohammedawi and H. Znad, *Biomass Bioenergy*, 2020, **134**, 105482.
70 E. Eroglu, U. Gunduz, M. Yucel and I. Eroglu, *Int. J. Hydrogen Energy*, 2011, **36**, 5895–5903.
71 G.-J. Xie, B.-F. Liu, H.-Q. Wen, Q. Li, C.-Y. Yang, W.-L. Han, J. Nan and N.-Q. Ren, *Int. J. Hydrogen Energy*, 2013, **38**, 7780–7788.
72 A. Pandey, K. Gupta and A. Pandey, *Biomass Bioenergy*, 2015, **72**, 273–279.
73 B. Liu, Y. Jin, G. Xie, Z. Wang, H. Wen, N. Ren and D. Xing, *ES Energy Environ.*, 2018, **1**, 56–66.
74 B. Liu, Y. Jin, Z. Wang, D. Xing, C. Ma, J. Ding and N. Ren, *Int. J. Hydrogen Energy*, 2017, **42**, 18279–18287.
75 A. Elreedy, M. Fujii, M. Koyama, K. Nakasaki and A. Tawfik, *Water Res.*, 2019, **151**, 349–361.
76 A. Mostafa, A. El-Dissouky, A. Fawzy, A. Farghaly, P. Peu, P. Dabert, S. Le Roux and A. Tawfik, *Bioresour. Technol.*, 2016, **216**, 520–528.
77 K. Anam, M. S. Habibi, T. U. Harwati and D. Susilaningsih, *Int. J. Hydrogen Energy*, 2012, **37**, 15436–15442.
78 J. Bu, H.-L. Wei, Y.-T. Wang, J.-R. Cheng and M.-J. Zhu, *Water Res.*, 2021, **202**, 117440.
79 S. Ghosh, S. Dutta and R. Chowdhury, *Energy Convers. Manage.*, 2020, **226**, 113549.
80 G. Policastro, A. Cesaro and M. Fabbricino, *Int. J. Hydrogen Energy*, 2023, **48**, 21038–21054.
81 Q. Zhang, Y. Wang, Z. Zhang, D.-J. Lee, X. Zhou, Y. Jing, X. Ge, D. Jiang, J. Hu and C. He, *Bioresour. Technol.*, 2017, **229**, 222–230.
82 K. Vasumathi, M. Premalatha and P. Subramanian, *Renewable Sustainable Energy Rev.*, 2012, **16**, 5443–5450.
83 J. Cai, Y. Zhao, J. Fan, F. Li, C. Feng, Y. Guan, R. Wang and N. Tang, *J. Biotechnol.*, 2019, **302**, 18–25.
84 M. Jin, X. Wei, X. Mu, W. Ren, S. Zhang, C. Tang and W. Cao, *Bioresour. Technol.*, 2024, **396**, 130429.
85 T. Zhang, D. Jiang, H. Zhang, Y. Jing, N. Tahir, Y. Zhang and Q. Zhang, *Int. J. Hydrogen Energy*, 2020, **45**, 3807–3814.
86 Y. Zhu, N. Zhang, Z. Liu, N. Liu, A. Sharma, G. Chen and Y. Yang, *Energy Convers. Manage.*, 2021, **238**, 114155.
87 J. G. Ferry and K. A. Kastead, *Archaea: Molecular and Cellular Biology*, 2007, pp. 288–314.
88 S. Toya, S. Iriguchi, K. Yamaguchi and T. Maeda, *Fermentation*, 2023, **9**, 943.
89 Y. Yang, K. Tsukahara, Z. Zhang, N. Sugiura and S. Sawayama, *Biochem. Eng. J.*, 2009, **44**, 131–135.
90 A. Xia, J. Cheng, R. Lin, J. Liu, J. Zhou and K. Cen, *Bioresour. Technol.*, 2013, **131**, 146–151.
91 R. Lin, J. Cheng, Z. Yang, L. Ding, J. Zhang, J. Zhou and K. Cen, *Bioresour. Technol.*, 2016, **214**, 686–691.
92 L. Ding, J. Cheng, H. Lu, L. Yue, J. Zhou and K. Cen, *Energy Convers. Manage.*, 2017, **148**, 394–404.
93 Y. X. Zhu, N. Zhang, Z. Y. Liu, N. Liu, A. Sharma, G. P. Chen and Y. N. Yang, *Energy Convers. Manage.*, 2021, **238**, 114155.
94 S. A. Neshat, M. Mohammadi and G. D. Najafpour, *Chem. Eng. J.*, 2018, **338**, 8–14.
95 J. Qian, Y. H. Zhang, P. F. Wang, B. H. Lu, Y. X. He, S. J. Tang and Z. Y. Yi, *Water Res.*, 2022, **217**, 118447.
96 C. Tada and S. Sawayama, *J. Biosci. Bioeng.*, 2004, **98**, 387–390.
97 S. A. Neshat, M. Mohammadi and G. D. Najafpour, *Chem. Eng. J.*, 2017, **330**, 616–624.
98 Q. Liu, H. Y. Zhang, S. Chen, Y. Q. Li, M. Mazarji, L. Feng, J. T. Pan, H. J. Zhou and C. M. Xu, *Chem. Eng. J.*, 2024, **490**, 151929.

99 C. Lu, G. Wang, Q. Zhang, X. Yang, J. Yu, T. Liu, F. Petracchini, Z. Zhang, Y. Sun and D. Jiang, *Appl. Energy*, 2023, **347**, 121463.
100 N. Zhang, C. Lu, Z. Zhang, H. Zhang, L. Liu, D. Jiang, K. Wang, S. Guo, J. Wang and Q. Zhang, *Bioresour. Technol.*, 2022, **345**, 126561.
101 T. Raj, K. Chandrasekhar, A. Naresh Kumar, J. Rajesh Banu, J.-J. Yoon, S. Kant Bhatia, Y.-H. Yang, S. Varjani and S.-H. Kim, *Bioresour. Technol.*, 2022, **344**, 126292.
102 P. R. Yaashikaa, M. Keerthana Devi and P. Senthil Kumar, *Int. J. Hydrogen Energy*, 2022, **47**, 41488–41506.