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Review of over two decades of research on dark and photo fermentation for biohydrogen production – A combination of traditional, systematic, and bibliometric approaches

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ABSTRACT

Biohydrogen represents a highly feasible and environmentally sustainable fuel alternative for the world's growing energy needs. However, technological advancements are still required for large-scale hydrogen utilization, particularly in determining the most advantageous technological path for recovering affordable and renewable hydrogen. Researchers have conducted numerous studies to determine the optimal technology for producing large-scale biohydrogen. However, no comprehensive systematic and bibliometric review presents an overview of the various production modes, i.e., the photo and dark fermentation techniques. This paper reviews recent research on biohydrogen production using dark and photofermentation modes, spanning over two decades, using Scopus data. The review highlights the growing push to integrate hydrogen production into larger bioenergy systems, focusing on improving the core processes and removing obstacles. Techniques like co-digestion and two-stage anaerobic digestion can increase production yields. The review also highlights the possibility of combining waste treatment with energy production to address environmental issues. Incorporating dark- and photo-fermentation processes in commercial hydrogen production shows greater potential for commercial use, potentially increasing yield. The study concluded by identifying challenges for the various modes of production and ways to overcome them. It also provided pertinent information on potential future research directions.

1. Introduction

Energy is essential to both modern life and industrial production. About 85% of the world's energy is produced and consumed is derived from fossil fuels such as natural gas, coal, and oil [1]. This heavy reliance on fossil fuels has contributed to both energy crises and environmental challenges [2,3]. To satisfy global energy demands, around 36 billion tonnes of carbon dioxide (CO_2) are emitted into the atmosphere annually [4]. According to Ref. [5], fossil fuels account for over 90% of these emissions. For this reason, it is critical to identify alternative clean energy sources to meet the global energy demands.

High-energy carrier hydrogen (H_2) emits no carbon emissions and only generates water as a byproduct, making it a clean fuel [6,7]. With an energy density of 140 MJ/kg, significantly higher than the 50 MJ/kg of traditional solid fuels, hydrogen is a promising energy carrier [8,9]. Nonetheless, grey hydrogen accounts for 96% of the production of hydrogen currently, which is produced through steam methane reforming and relies on non-renewable fossil fuels [10]. The main pathways for producing hydrogen through biological means are dark fermentation, photolysis, photo fermentation, and microbial electrolysis cells. These pathways are more sustainable and economically viable than other approaches [9,11]. Microorganisms can produce hydrogen from a readily available and renewable feedstock, making biological hydrogen production strategies a viable alternative to chemical

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approaches like reforming and gasification. Taken together, these strategies may contribute to hydrogen production on a large-scale. Farm wastes [12], food wastes [13], and wastewater from industrial operations like cheese making [14], sugar refining [15], and olive processing [16] are all useful sources of feedstock for the biohydrogen generation process [17].

Researchers have used different review procedures (i.e., conventional or bibliometric) to assess work progress within the hydrogen sector. For instance, the conventional review approach was used to review hydrogen production and use [18], chemical-looping technology for producing hydrogen [19], hydrogen production methods [20], bio-hydrogen generation using various dark and photo-fermentation operating modes [21,22], strategies to increase the biological process's ability to produce biohydrogen [23], and, various organic biomasses, as well as their potential for producing biohydrogen in systems at the pilot-scale and laboratory levels [24]. Others also employed the bibliometric approach to review studies on hydrogen production, and this includes production of hydrogen through dark fermentation [25], production of biohydrogen through catalysis using organic waste materials [26], sludge fermentation's potential to produce hydrogen [27], the application of nanotechnology in the production of dark fermentative biohydrogen [28], thermochemical and biological pathways for the production of hydrogen [29], and hydrogen fuel cells [30].

The systematic and bibliometric review method from the existing literature has not been used in a full study to look at the progress and trends of research on dark and photo fermentative processes. A thorough bibliometric analysis is essential to grasp the field's state properly, spot new directions, and investigate the possibilities of dark and photo fermentation to biohydrogen production. The objective of this current study is to provide a comprehensive overview of over two decades of research on dark and photo fermentation, as well as the challenges and directions for future research. This paper goes beyond simply compiling the body of knowledge; instead, it painstakingly creates an extensive summary suited explicitly for future research projects. By pointing out gaps in the current literature and outlining possible research avenues, this review provides researchers with a strategic road map to help them navigate and actively participate in the developing field of dark and photo fermentation for biohydrogen production. The research gains scholarly depth by incorporating a thorough bibliometric analysis using the Biblioshiny tool. The paper offers an accurate visual depiction of the research landscape by distinguishing historical and current research emphases, identifying noteworthy contributors, the geographic distribution of research, and identifying emerging trends.

The paper is ordered in the following manner: Section 2 provides a brief overview of dark and photo fermentation, Section 3 presents the analysis method, and Section 4 showcases the results, discussion, and future research directions. The final section, i.e., section 5, provides the conclusion.

2. Brief overview of dark and photo fermentation

This section provides a brief description of the dark and photo fermentation processes as well as a comparison between the two techniques.

2.1. Dark fermentation

The use of obligate or facultative anaerobic bacteria, such as *Enterobacter*, *Clostridium*, *Escherichia coli*, and *Bacillus*, is known as dark fermentation (DF) or anaerobic fermentation to produce hydrogen from organic carbon substrates, as presented in Figs. 1 and 2. These equations characterize the route [31]:

$$Glucose \xrightarrow{Glycolysis} Pyruvate \tag{1}$$

$$Pyruvate + Co - A + 2Fd(ox) \xrightarrow{Reduction} Acetyl\ Co - A + 2Fd(red) + CO_2 \tag{2}$$

$$2Fd(red) \underset{Hydrogenase}{\overset{Oxidation}{\rightarrow}} 2Fd\ (ox) + H_2 \uparrow \tag{3}$$

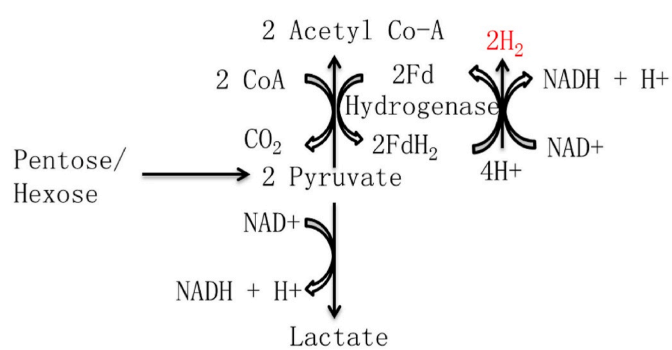

Fig. 2. Diagram showing the facultative anaerobe's hydrogen production pathway [32].

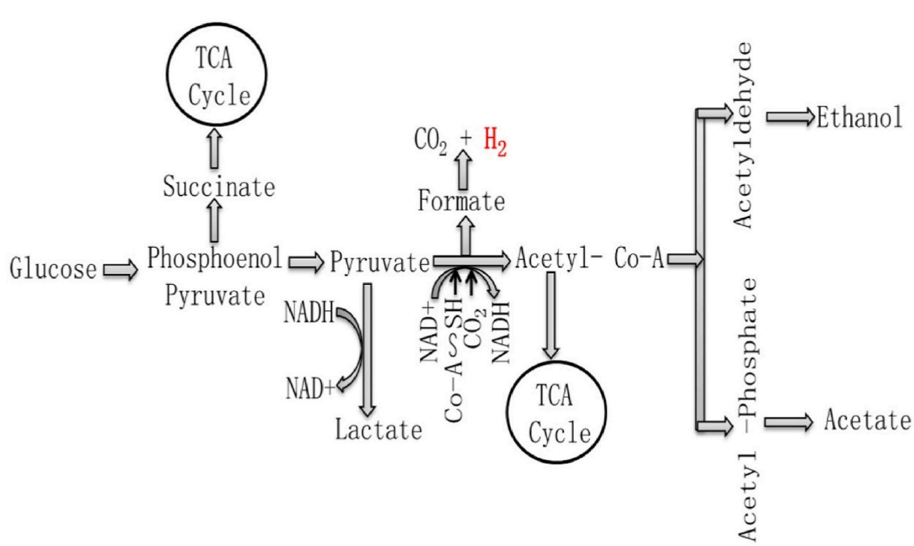

Fig. 1. A schematic demonstration of the strict anaerobe's hydrogen production pathway [32].

Biomass, produced through photosynthesis, stores biochemical energy. It provides the fermentative microbes with nourishment to perform their various metabolic functions. There has been much research on dark fermentation, which produces H_2 and simple organic acids from biomass, utilizing pure carbon sources or other organic biomasses. In this environmentally friendly and cost-effective process, pure sugars and organic wastes serve as substrates for biohydrogen production. In order to increase their metabolic energy and biomass, bacteria growing on organic substrates experience oxidative degradation in a process known as dark fermentation. The anaerobic oxidation of substrates generates and removes electrons by reducing protons into H_2, thereby maintaining the cell's electrical neutrality [33]. In most cases, DF generates H_2 at a high rate that is light-independent [17].

Process variables like pH, HRT, and gas partial pressure greatly affect these bacteria's ability to make hydrogen because they change metabolic balance. Therefore, the end products of fermentation that a bacterium produces depend upon the environment in which it grows. Unreleased gaseous hydrogen is present in reduced fermentation end products such as lactate, butanol, and ethanol [33]. The bacterium's metabolism must be switched from reducing acids (lactate) and alcohols (ethanol, butanol) to volatile fatty acids (VFA) to maximize the yield of H_2. Although *C. pasteurianum* is a well-known producer of VFA and H_2, its metabolism can be steered away from H_2 production and toward the production of solvents by limiting Fe concentrations, CO (which inhibits Fe-hydrogenase), and high glucose concentrations (12.5% w/v) [34,35]. Many investigations on DF by anaerobic fermentative bacteria, such as *Escherichia coli* [36–38], *Clostridium* [39–45], and *Enterobacter* [46–49], have been conducted. Numerous authors have documented H2 production from mixed microflora derived from various sources, including heat-treated anaerobic sludge [50–52] and cow dung [53–57], has been documented by numerous authors. Several elements, such as the kind of organism, the metabolic pathway taken, the type of substrate utilized, and the final products generated, influence how much H_2 is produced during DF.

2.2. Photo fermentation

Since its discovery by Gest and Kaman in 1949, biohydrogen production via photo fermentation utilizing photosynthetic bacteria has demonstrated an efficient way to produce high-purity hydrogen without producing oxygen [58,59]. Anaerobic or photosynthetic bacteria, such as strains of *Rhodopseudomonas, Rhodobium, Rhodobacter*, and Rhodospirillum, break down organic compounds in the presence of light energy during the photo-fermentation process, and nitrogenase catalyzes the reaction to produce biohydrogen [60]. The light energy, whether artificial or natural, is a crucial component of the entire process. Purple non-sulfur (PNS) bacteria are the most common photosynthetic bacteria used. In addition, rare green and purple bacteria are employed. Light energy is utilized to oxidize the carbon source and create electrons. PNS bacteria and other suitable bacteria produce enzymes such as hydrogenase or nitrogenase. Nitrogenase is the primary enzyme responsible for hydrogen formation. The process operates under anaerobic conditions. **Eq. (4)** describes how nitrogenase uses electrons and ATP (adenosine triphosphate) to produce hydrogen and ADP (adenosine diphosphate) in anaerobic conditions [61].

$$2H^+ + 2e^- + 4ATP \rightarrow H_2 + 4ADP + P_i \tag{4}$$

The particular bacteria employed and the converted carbon source are the primary determinants of the environmental factors (temperature, pH, and light intensity). The ideal range for pH is 6.8–7.5, for temperature is 30–35 °C, and for light intensity is 6–6000 lux [32,61]. Aside from molecular hydrogen, photo fermentation also produces trace amounts of CO_2. **Eq. (5)** illustrates a photo fermentative reaction with PNS bacteria and acetate as the organic source [61]. Fig. 3 displays the PNS bacterial pathway for producing hydrogen.

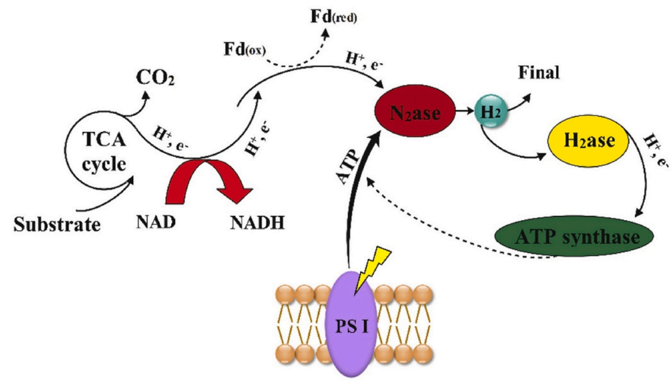

Fig. 3. PNS bacterium photo fermentation pathway for hydrogen production [62].

$$2CH_3COOH + 2H_2O \rightarrow 4H_2 + 2CO_2, \Delta G_0 = +104\ kJ \tag{5}$$

As previously indicated, the nitrogenase enzyme is used by PNS bacteria to produce hydrogen through photo fermentation. This enzyme's metabolism is heavily dependent on N_2 molecules. According to **Eq. (6)**, nitrogenase catalyzes the nitrogen-fixation reaction in the presence of N_2, resulting in hydrogen as a byproduct. Additionally, the release of ammonia inhibits nitrogenase activity [63].

$$N_2 + 8e^- + 8H^+ + 16ATP \rightarrow 2NH_3 + H_2 + 16ADP + 16P_i \tag{6}$$

In the absence of N_2, the nitrogenase shifts from nitrogen fixation to **Eq. (7).** Four hydrogen molecules are formed by this reaction [62,63].

$$8e^- + 8H^+ + 16ATP \rightarrow 4H_2 + 16ADP + 16P_i \tag{7}$$

Even though the two reactions mentioned above require a significant amount of intracellular energy (ATP), an environment lacking nitrogen can change all protons into the preferred product [64]. In recent times, photofermentation has emerged as a prominent global research focus for hydrogen production, mainly due to its extensive substrate consumption and wide range of available raw materials [65]. Furthermore, this process can produce a significant amount of hydrogen at room temperature and pressure, making it very effective and safe for the environment.

Numerous studies have explored the optimal light intensity for achieving high hydrogen yield in photo fermentative bacterium (PNS) cultures. For instance, Ref. [66], isolated Rhodobacter sphaeroides KKU-PS5, a purple non-sulfur photosynthetic bacterium, from an upflow anaerobic sludge blanket bioreactor to enhance methane production. While malate is the preferred carbon source, the strain KKU-PS5 can grow and produce hydrogen using a variety of sugars. Additionally, it uses Aji-L and glutamate as an inexpensive nitrogen supplement to produce photo-biohydrogen. The study found that an initial pH of 7.0, a FeSO4 concentration of 4 mg/L, a temperature of 30 °C, and a light intensity of 6 klux are the optimal conditions for hydrogen production from malate. The maximum levels of hydrogen production, yield, and hydrogen production rate (HPR) were achieved under these parameters.

In contrast to continuous illumination, hydrogen production during a dark/light cycle resulted in lower HY and HPR. The highest hydrogen production rates were 11.08 ml H_2/L and 3.80 mol H_2/mol malate. Luongo et al.'s [67] study investigated the effects of an initial pH of 6.0, a temperature of 25 °C, and illumination at 4000 lux on the production of hydrogen and poly-β-hydroxybutyrate (PHB) from dark-fermented municipal waste. They used a mixed consortium and *Rhodobacter sphaeroides* AV1b as inoculums. They used a mixed consortium and *Rhodobacter sphaeroides* AV1b as inoculums. The results revealed varying hydrogen productivities, indicating a potential role for a mixed consortium. The integrated process allows for the simultaneous presence of dark-fermentative and photo-fermentative bacteria with diverse nutrient and metabolic requirements within a single reaction system.

This approach can potentially reduce both the costs and reactor volume associated with hydrogen production, optimizing hydrogen yield while removing COD from dark-fermented effluent. Tests involving *Rhodobacter sphaeroides* and a mixed culture consortium recorded hydrogen productivities of 364 and 559 N ml H_2 L^{-1}, respectively, with the PNSB consortium producing 1.5 times more hydrogen than the pure culture. However, the mixed culture yielded only 55 mg of PHB per gram of COD, while the *Rhodobacter sphaeroides* culture produced 155 mg of PHB per gram of COD. Notably, the concurrent production of H_2 and PHB was associated with a dissolved COD removal rate exceeding 80% in all tests.

2.3. A brief comparison between the DF and photo fermentative processes

Using two distinct types of microbes, such as photosynthetic and fermentative, is a promising way to produce biohydrogen. Biohydrogen will be produced using photo fermentation and DF modes, respectively, with the aid of these microbes. The potential use of waste waters and organic wastes by anaerobic bacteria with a higher rate of producing hydrogen than other processes like photo fermentation and photolysis makes DF one of the processes that attracts the most attention. Alternatively, photosynthetic PNS bacteria—which can grow in a photoheterotrophic, photoautotrophic, or chemoheterotrophic manner—are examples of extremophiles that carry out the photo fermentation process [68,69]. When bacteria are photoheterotrophic, they produce hydrogen in an anaerobic environment with light and an organic electron donor. Both green algae and photosynthetic bacteria use light-dependent biohydrogen production technologies, and both depend heavily on the enzymes hydrogenase and nitrogenase [69,70].

2.4. An integrated method for producing hydrogen through fermentation

It is commonly known that short chain organic acids and alcohols are created in large quantities during DF and that bacteria involved in photo fermentation can additionally transform these acids to produce more hydrogen, maximizing the total yield of H_2 and the single substrate's conversion efficiency [15]. There are currently two main approaches to integrating DF with photo-fermentation processes: a sequential and an integrated process. The research conducted by Ref. [71] showed that the integrated process, which allows dark-fermentative and photo-fermentative bacteria to coexist with varying nutrient and metabolic types within a single reaction system, reduced the costs and reactor volume of hydrogen production systems. This study combined C. butyricum and *RLD-53* in ratios of 1:100, 1:200, 1:300, 1:400, 1:500, and 1:600. The mixed culture of *C. butyricum* and *R. faecalis RLD-53* yielded the highest hydrogen production when the population ratio of the two bacteria was 1:600, with a recorded maximum yield of 122.4 ml-H_2 per vessel and a daily hydrogen production rate of 0.5 ml-H_2 per ml of culture. The results indicated that a significant drop in the system's pH restricted the growth of photofermentative bacteria. To further investigate the effects of various operational parameters on hydrogen production, including phosphate buffer, substrate concentration, initial pH, light intensity, and bacterial ratios, the study by Ref. [72] utilized immobilized *R. faecalis RLD-53* alongside mixed cultures of *C. butyricum* grown on glucose. A pH of 7.5, a ratio of 1:10 for dark to photo bacteria, and an intensity of 8000 lux of light were found to yield the highest amount of hydrogen. A 33.85 ml H_2/l/h was the highest rate of hydrogen production. Phosphate buffer concentration was the most important factor since it raised the acetate to butyrate ratio in soluble metabolites from *C. butyricum*.

However, a sequential process is easier to run and manage because the two types of bacteria can operate independently in their ideal environments. A study by Ref. [73] used an ethanol-type fermentative *Ethanoligenenes harbinese* B49 and an immobilized *R. faecalis RLD-53* to test the efficiency of sequential H_2 production. According to these findings, phosphate buffer may improve the strain *R. faecalis* RLD-53's acid tolerance and H_2 yield, rising to 6.32 mol-H_2/molglucose.

A significant improvement in H_2 yield can be achieved by using the intermediate VFA produced during DF as a substrate in photofermentation for the production of H_2 by PNS bacteria. Sequential dark fermentation followed by photofermentation is a more efficient method of increasing H_2 yield than single-stage dark or photofermentation, which requires two distinct reactors for each process, making control and optimization of each process simple [74]. In an integrated system, the two essential enzymes, nitrogenase and hydrogenase, mediate the biological production of H_2. HUPEcoded is the classification given to hydrogenase enzymes. Hydrogenases that uptake [NiFe], with a hex encoding, are classified as bidirectional (NiFe-bidirectional), FeFe, NiFeSe, and Fe-only [17]. Aerobes and facultative anaerobes contain NiFe hydrogenases, while strict anaerobes only have Fe-only hydrogenases. The nitrogenase enzyme catalyzes PNS bacteria's production of photofermentative H_2 [75].

3. Methodology

The bibliometric analysis utilized data on scientific output from Scopus, one of the largest databases for peer-reviewed articles. Scopus has over 23,452 peer-reviewed journals, of which 5500 are fully open-access and comprise more than 77.8 million core records. Launched in 2004 by the Dutch information and analytics company Elsevier, Scopus is a widely recognized source for comprehensive academic research [76,77]. The following search terms were used to retrieve data: ("hydrogen energy" OR "biohydrogen" OR "hydrogen" OR "hydrogen production" OR "hythane" OR "biohythane") AND ("dark photo fermentation" OR "anaerobic digestion"). The search covered the period from 2000 to 2023, yielding an initial result of 4710 documents. We further refined the search by limiting the subject areas to chemical engineering, energy, engineering, genetics, biochemistry, chemistry, molecular biology, and agricultural and biological sciences, resulting in 3398 documents. We then filtered the document types only to include articles and conference papers, which reduced the total to 2908. After restricting the language to English, the final dataset comprised 2838 documents. We then conducted a detailed screening of titles and abstracts to exclude 244 out-of-scope documents. Ultimately, this study used 2594 documents for systematic and bibliometric analysis.

According to Refs. [78–80], bibliometric analysis is a quantitative method of analyzing academic literature that uses bibliometric data to describe, assess, and track published research in a given field of study. We conducted the bibliometric analysis using the open-source Biblioshiny program from RStudio. Biblioshiny is superior to other bibliometric tools because it offers a comprehensive set of statistical methods and visualizations that allow for conceptual mapping of the field of study and performance analysis [81–83].

4. Results and discussion

The results of the bibliometric analysis on hydrogen production from photo and dark fermentation are shown in this section. The following bibliometric analysis was performed and comprehensively discussed in this section: (i) publication metrics overview and articles published annually, (ii) country-specific production, collaborations, and corresponding authors countries, (iii) keywords and trend topics, (iv) conceptual structure (thematic evolution, thematic map, and factorial analysis), (v) authors productivity, citations, journals, and affiliations.

4.1. Publication metrics overview and articles published annually

Fig. 4 shows the publication metrics on hydrogen production via dark and photo fermentation from 2000 to 2023. It can be seen that the field has produced 2594 documents from 411 sources, with 7033 authors and an annual growth rate of 11.43%. The average of 4.87 co-authors per document and 26.95% international co-authorship rate indicate solid collaborative efforts, both domestically and globally. It is

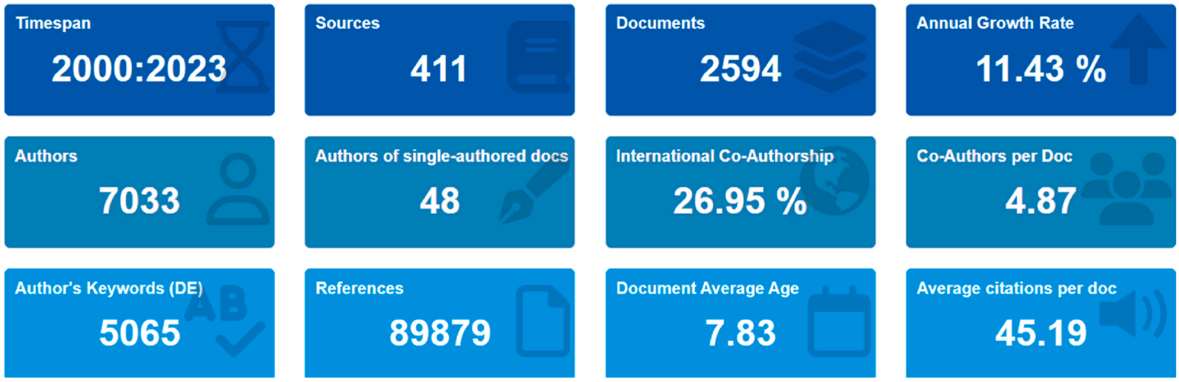

Fig. 4. Research metrics overview.

worth mentioning that the research field appears well-grounded, with an average of 45.19 citations per document and 89879 references across all publications. The presence of 5065 unique author keywords suggests a variety of subtopics and approaches within the field. Although the average document age of 7.83 years implies a balance between foundational work and ongoing innovation, the high citation rate highlights this research's significant impact and relevance. These metrics collectively portray a mature yet dynamic field that continues to attract substantial interest and investment, likely driven by the potential applications of dark and photo fermentation in sustainable hydrogen production. The results suggest a research area characterized by interdisciplinary collaboration, global engagement, and high scientific impact, with promising implications for future advancements in hydrogen production.

Fig. 5 shows the annual article production in the research field from 2000 to 2023. The results show a substantial upward trend in research output over these 24 years. For instance, starting with 18 articles in 2000, the field experienced modest growth in the early years, with some fluctuations. The year 2002 saw a slight increase to 20 articles, followed by a dip to 17 in 2003. Nevertheless, 2004 marked a notable jump to 28 articles, indicating growing interest in the topic. The subsequent years showed steady progress, with 2006 and 2007 surpassing 40 articles annually. A substantial leap occurred in 2008, with 74 articles published, nearly doubling the previous year's output. This surge suggests a crucial moment, possibly due to technological advancements or growing awareness of the potential of dark photo fermentation for hydrogen production.

The momentum continued into 2009 and 2010, with 66 and 84 articles, respectively. The year 2011 marked another significant milestone as the annual output exceeded 100 articles for the first time, reaching 101. This breakthrough demonstrates the maturing of the research area and its establishment as a prominent topic within the broader renewable energy and biotechnology field. In the following years, they maintained this high level of productivity, with slight fluctuations but a general upward trend. Notable increases were observed in 2014 (135 articles) and 2015 (169 articles), indicating sustained interest and possibly breakthroughs or applications driving research. The period from 2016 to 2019 saw some variability but maintained a high output level, ranging from 142 to 186 articles per year. The year 2020 marked the beginning of another surge in research activity, with 215 articles published, possibly influenced by increased focus on sustainable energy solutions in response to global challenges. This upward trajectory continued in 2021 and 2022, reaching peak production with 234 and 245 articles, respectively.

Dark photo fermentation, a technology for renewable energy production, has seen a steady growth in article production over two decades, with significant increases in recent years. This indicates a dynamic field with continuous discoveries and innovations driving further exploration. The slight decrease in 2023 may reflect a shift towards more focused, high-quality research or the beginning of a consolidation phase where practical applications and scalability become key focus areas. This trend suggests dark photo fermentation has moved from a niche research topic to a mainstream area of investigation within renewable energy studies, likely due to a growing global emphasis on clean energy technologies and reducing fossil fuel dependence.

4.2. Country-specific production, collaboration, and corresponding authors countries

The total number of articles published per country is displayed in

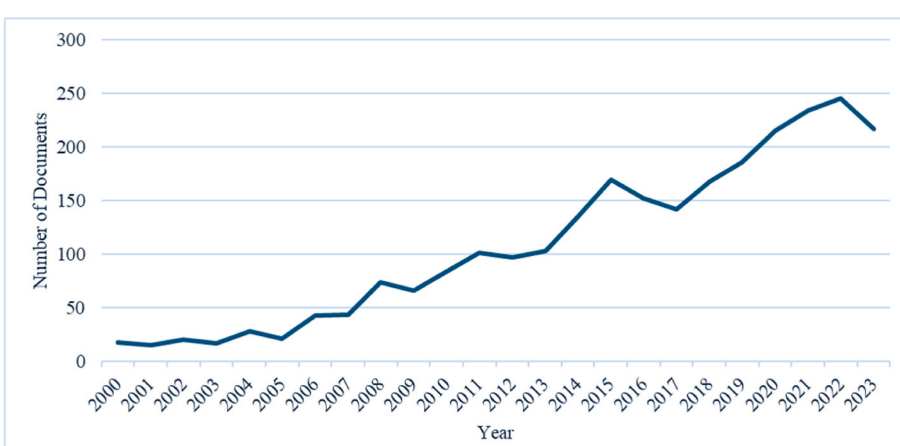

Fig. 5. Annual scientific production.

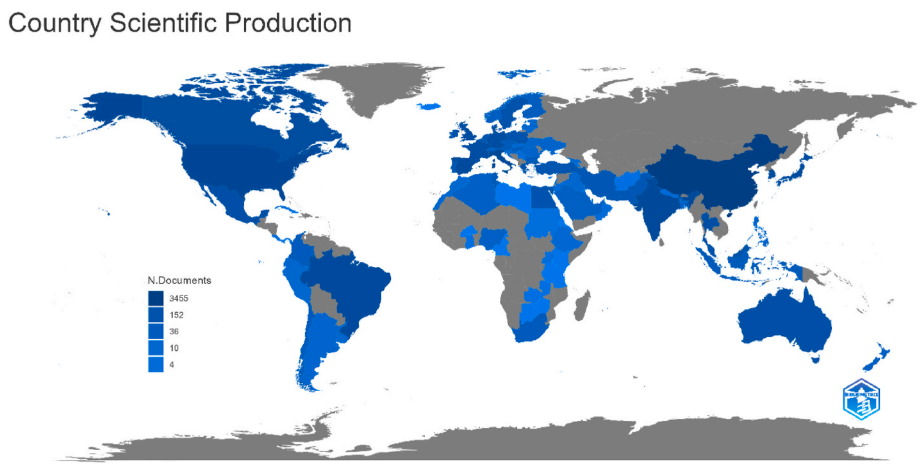

Fig. 6. Country scientific production.

Fig. 6. The results indicate that China emerges as the top publishing country with 3455 publications, outshining other countries. The United States follows with 808 publications, while Italy lags just behind with 738 articles. India, Brazil, Spain, Japan, and South Korea form the next tier, each publishing between 400 and 600 articles, demonstrating their outstanding contributions to the field. Canada and the United Kingdom round out the top ten, with around 400 publications each. It can be observed that there is a concentration of research in East Asia, North America, and Europe, with China, the USA, and several European countries dominating the top positions. This distribution suggests that these regions are at the forefront of developing and implementing dark photo fermentation technology for hydrogen production. The significant gap between China and other countries implies that China may have a considerable advantage in knowledge, expertise, and potential commercialization of this technology. In view of this, the government has invested hugely in green hydrogen production [84,85]. A recent survey by Global Times revealed that China has invested more than $42.04 billion in green hydrogen, positioning itself as the global leader in this sector [85].

Middle-ranking countries like Germany, France, Denmark, Thailand, and Mexico, with published articles varying from 250 to 350, demonstrate moderate engagement in the field. The presence of emerging economies like India and Brazil among the top contributors highlights the global interest in this renewable energy solution and its potential for addressing energy needs in diverse economic contexts. Countries in the lower half of the list, particularly those with fewer than 100 publications, may be disadvantaged regarding technological readiness and may need to increase their research efforts to remain competitive in the future hydrogen economy. It can be observed that several African countries, with a few exceptions like Egypt, Tunisia, and South Africa, have limited research output in this area, suggesting a potential gap in hydrogen production via dark-photo fermentation on the continent.

Countries with higher publication counts will likely have more advanced infrastructure, skilled researchers, and potentially more favorable policies supporting dark photo fermentation research. This could lead to faster technological breakthroughs, more efficient hydrogen production methods, and earlier adoption of hydrogen as a clean energy source. The disparity in research output may also impact future economic opportunities related to hydrogen technology, with leading countries potentially gaining advantages in patents, commercialization, and export of related technologies. Furthermore, the research concentration in certain regions may necessitate increased international cooperation to ensure global access to this promising clean energy technology, particularly for developing nations with lower research output.

Fig. 7 presents collaboration between countries on hydrogen production using dark fermentation. The map depicts countries in blue actively engaged in this field, with red lines connecting collaborating nations. As seen, there is a high concentration of collaboration among North American, European, and East Asian countries, signifying these regions are at the lead of dark photo fermentation research. The United States, China, and several European nations appear to be central hubs,

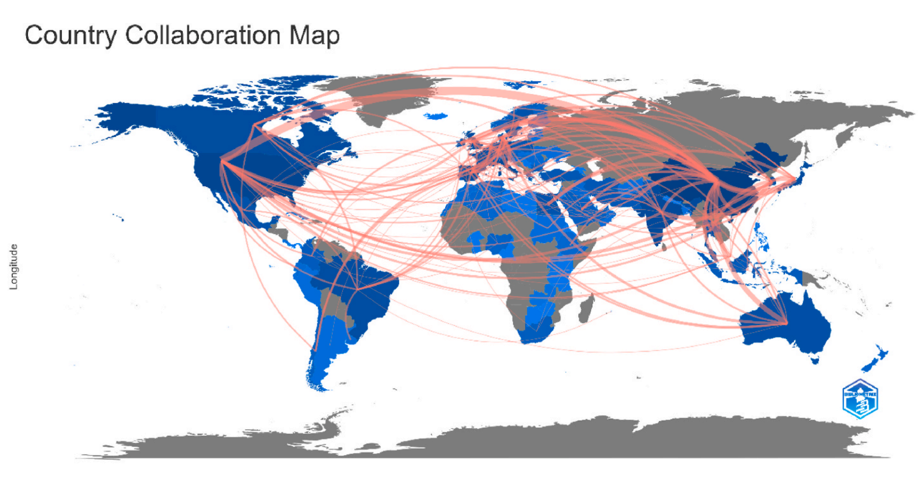

Fig. 7. Collaboration between countries.

connecting with numerous partners worldwide. This indicates their significant role in advancing technology and fostering international cooperation. The map also shows involvement from countries in South America, Africa, and South Asia, although with fewer connections, pointing to potential areas for expanded collaboration. The global nature of this research network highlights the universal interest in developing sustainable hydrogen production methods, likely driven by the pressing need for clean energy solutions to combat climate change. However, the varying degrees of connectivity suggest disparities in research capabilities or resources among nations. Future research could focus on strengthening collaborations with less connected countries to promote knowledge transfer and accelerate global progress in this field.

Additionally, investigating the specific nature of these collaborations - such as shared methodologies, technology transfer, or joint pilot projects - could provide valuable insights. Exploring ways to bridge the gap between highly connected and less connected regions could lead to more inclusive and comprehensive advancements in dark photo fermentation technology. Furthermore, analyzing the correlation between collaboration intensity and technological breakthroughs could help optimize future research strategies and resource allocation in this promising area of renewable energy research.

Fig. 8 illustrates the corresponding authors' countries. It can be observed that China emerges as the leader in this field, with an outstanding 393 single-country publications (SCP) and 167 multiple-country publications (MCP). This implies that China is strong in domestic research and has significant international collaborations. The United States is the second most productive country, with a lower output of 110 SCP and 36 MCP. India, Italy, and Brazil round out the top five countries in terms of SCP, with 94, 90, and 70 publications, respectively. It is worth highlighting that although these countries maintain high SCP counts, their MCP numbers are comparatively lower. This indicates a more nationally focused research approach. Spain and Canada show similar patterns with strong SCP counts and moderate MCP involvement.

Asian countries such as Korea and Japan also feature prominently in the figure, with Japan having a higher proportion of MCP than its SCP count. European countries, comprising the United Kingdom, Germany, and Denmark, show varying research output and collaboration patterns. Denmark, in particular, stands out with its unusually high MCP count compared to its SCP. Countries like Mexico, France, and Greece demonstrate more modest research outputs but still contribute significantly to the global knowledge of hydrogen production through dark photo fermentation. Australia, Sweden, and Malaysia round out the list with balanced SCP and MCP counts. This indicates active participation in domestic and international research efforts. The findings highlight the global nature of this research area, with contributions coming from several geographical regions. The dominance of China in both SCP and MCP suggests its potential leadership role in advancing this technology, which could have significant implications for future energy policies and technological developments. The varying ratios of SCP to MCP across countries indicate differing approaches to research collaboration, which may be influenced by factors such as national research policies, funding structures, and scientific infrastructure. Countries with higher proportions of MCP, like Denmark and Japan, may benefit from knowledge transfer and resource sharing through international partnerships.

Conversely, countries with higher SCP counts might focus on building domestic expertise and infrastructure. The results also suggest potential opportunities for increased global collaboration, particularly for countries with low MCP counts relative to their SCP output. Such collaborations could lead to more diverse and innovative approaches to solving challenges in hydrogen production through dark photo fermentation. Furthermore, the global distribution of research efforts in this field indicates its perceived importance across various nations, potentially reflecting a widespread recognition of the need for sustainable energy solutions. This global interest could accelerate advancements in hydrogen production technology, contributing to efforts to mitigate climate change and reduce dependency on fossil fuels.

4.3. Keywords and trend topics

The word cloud based on author keywords is displayed in Fig. 9. It can be seen that the most frequent term, "anaerobic digestion," highlights its fundamental role as the core process. This is closely followed by "biogas" and "hydrogen," indicating the primary products of interest. The high frequency of "methane" and "biohydrogen" further emphasizes the dual focus on these two valuable biogases. The prominence of "food waste" pinpoints a significant trend towards utilizing waste materials as substrates, aligning with circular economy principles [86,87]. "Dark fermentation" and "hydrogen production" directly relate to the specific process of interest, while "microbial community" and "volatile fatty acids" point to the importance of understanding and optimizing the biological aspects of the process. The frequent occurrence of terms like "co-digestion," "anaerobic co-digestion," and "two-stage anaerobic digestion" suggests a strong interest in process integration and optimization strategies. "Waste activated sludge" and "sewage sludge" indicate a focus on wastewater treatment applications, combining environmental remediation with energy production. The presence of "pretreatment," "hydrolysis," and various inhibition-related terms (e.g., "ammonia inhibition" and "hydrogen sulfide") indicates ongoing efforts to enhance process efficiency and overcome operational challenges. The inclusion of modeling terms ("ADM1″ and "mathematical modeling") suggests a growing emphasis on predictive tools and process understanding.

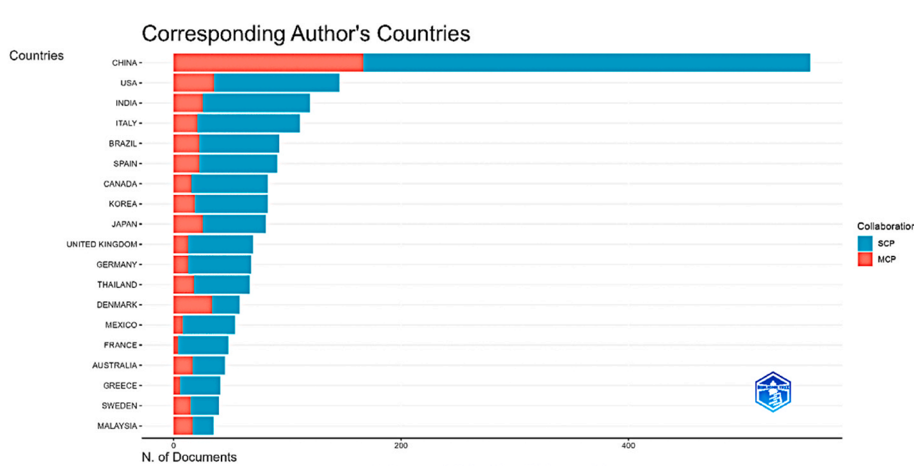

Fig. 8. Corresponding authors' countries.

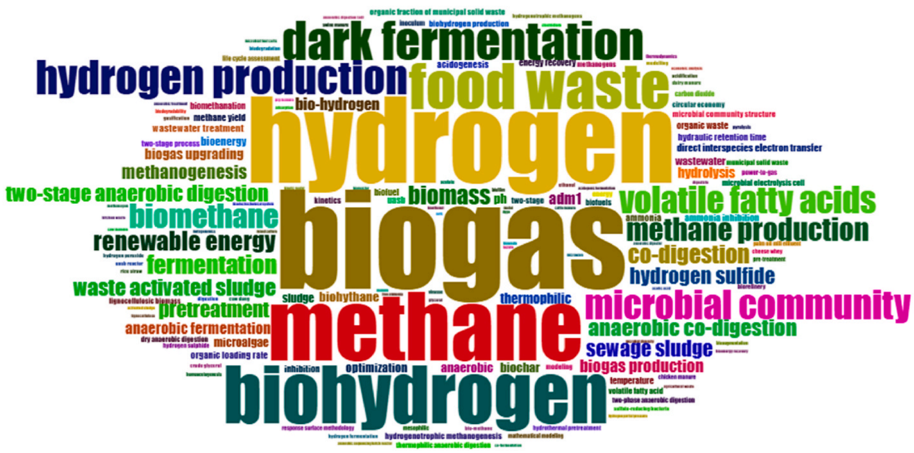

Fig. 9. Word cloud of author keywords.

Sustainability-related terms like "renewable energy," "bioenergy," and "circular economy" contextualize the research within broader environmental goals. The diversity of substrates mentioned (e.g., "microalgae," "lignocellulosic biomass," "cheese whey") indicates the exploration of various feedstocks for hydrogen production. Process parameters such as "pH," "temperature," and "organic loading rate" feature prominently, highlighting the importance of operational optimization. The implications of these results are significant. They suggest a mature field with a strong foundation in anaerobic digestion, actively exploring ways to enhance hydrogen production through process integration, substrate diversification, and operational optimization. The focus on waste materials as substrates indicates a push towards more sustainable and economically viable processes. The presence of advanced topics like "direct interspecies electron transfer" and "microbial electrolysis cell" points to cutting-edge research aimed at improving process efficiency. The frequency of terms related to methane alongside hydrogen suggests that researchers are considering holistic approaches to bioenergy production rather than focusing solely on hydrogen. This comprehensive approach, combined with the emphasis on modeling and process understanding, indicates a field that is not only advancing technologically but also deepening its theoretical foundations. Life cycle assessment and economic analysis terms suggest growing attention to these technologies' practical implementation and scalability.

Fig. 10 shows the trend topics within the study period. It can be seen that life cycle assessment, biomethane, and two-stage anaerobic digestion are the most prominent trends, which show significant growth in terms of frequency towards the end of the period. This suggests an increasing focus on sustainability analysis, biogas upgrading to biomethane, and process optimization through two-stage systems. The increase in life cycle assessment studies indicates a growing emphasis on assessing anaerobic digestion technologies' environmental impact and sustainability. Biomethane's prominence suggests the industry's shift towards producing higher-value, grid-injectable renewable natural gas. The increased interest in two-stage anaerobic digestion points to efforts to enhance process efficiency and stability by separating the acidogenesis and methanogenesis phases. Food waste is a significant topic, highlighting its importance as a feedstock for anaerobic digestion and aligning with global efforts to reduce organic waste in landfills. Anaerobic digestion shows a strong and consistent presence throughout the period, emphasizing its fundamental role in waste treatment and renewable energy production. Biogas, an essential product of anaerobic digestion, maintains relevance, though its relative importance seems to plateau in recent years, possibly due to the shift towards biomethane.

Co-digestion is a notable topic, indicating research into combining multiple feedstocks to improve process performance and economics. Fermentation and adm1 (Anaerobic Digestion Model No. 1) show moderate but consistent interest, signifying ongoing work in understanding and modeling the biochemical processes. Methanogenesis, the final stage of anaerobic digestion producing methane, maintains steady research attention. Topics like UASB (upflow anaerobic sludge blanket) reactors, bio-hydrogen production, and anaerobic treatment show varying interest over time, signifying evolving research priorities. Dairy manure appears as a specific feedstock of interest, likely due to its abundance and potential for on-farm energy production. Sucrose and

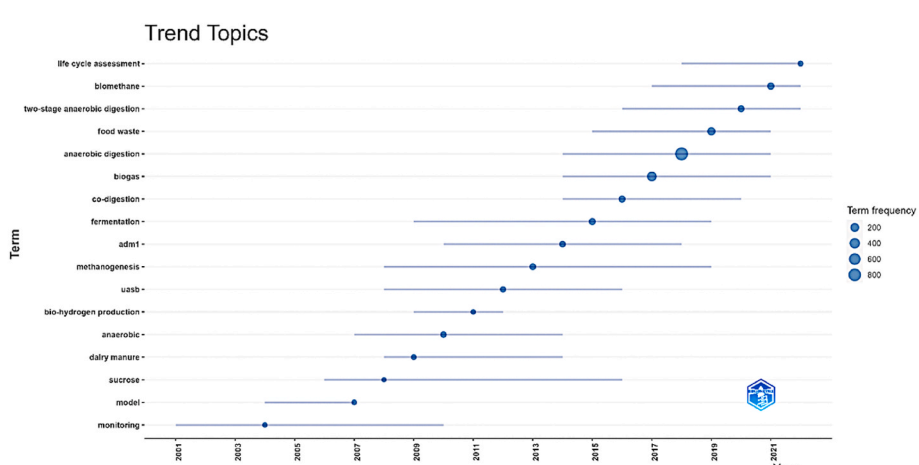

Fig. 10. Trends topics.

modeling show earlier peaks, possibly indicating shifts in research focus over time.

4.4. Conceptual structure

Thematic evolution of research topics in Fig. 11 shows significant focus shifts and emerging trends over time. In the 2000–2010 period, research predominantly focused on fundamental aspects of anaerobic digestion, including mathematical modeling, ADM1, municipal solid waste treatment, UASB reactors, anaerobic fermentation, co-digestion, biogas production, and food waste management. This era also saw interest in hydraulic retention time, methanogenesis, sludge treatment, and biohydrogen production, indicating a broad exploration of process parameters and potential products. The 2011–2020 decade marked a shift towards more specific and advanced topics, with hydrogen, anaerobic digestion, biogas upgrading, thermophilic processes, and hydrogen production gaining prominence. This transition suggests an increased focus on optimizing anaerobic digestion for diverse outputs, mainly hydrogen and upgraded biogas, and exploring high-temperature processes for enhanced efficiency. The most recent period, 2021–2023, shows a further evolution and specialization of research interests. Wastewater treatment, dry anaerobic digestion, and biofuel production are vital themes, demonstrating a growing emphasis on resource recovery and circular economy principles. The appearance of topics like acidogenesis, food waste, direct interspecies electron transfer, and biogas upgrading highlights ongoing efforts to understand and enhance anaerobic digestion's fundamental biochemical processes while improving end-product quality. New entries such as biomethane, thermophilic processes, and sugarcane biorefinery energy emphasize the diversification of feedstocks and the integration of anaerobic digestion into broader biorefinery concepts.

Fig. 12 displays the thematic map categorized into four quadrants: basic themes, motor themes, niche themes, and emerging/declining themes. As seen, the basic themes' quadrant contains "anaerobic digestion," "biogas," "food waste," "hydrogen," "methane," and "biohydrogen." These themes represent the foundational concepts and widely studied areas in hydrogen production from dark photo fermentation. Their position indicates high relevance (centrality) but lower development, suggesting they are well-established topics that remain important but may not be at the forefront of current research efforts. The presence of "food waste" in this quadrant highlights the ongoing interest in utilizing waste materials for sustainable energy production.

The clustering of hydrogen-related terms (hydrogen, biohydrogen) with methane and biogas indicates the interconnected nature of these renewable energy sources in the context of anaerobic processes. Moving to the motor themes, the quadrant, as seen, contains "anaerobic co-digestion," "biogas production," and "organic loading rate." These themes are characterized by high relevance and development, signifying that they drive the field forward. The prominence of anaerobic co-digestion suggests a focus on optimizing substrate mixtures to enhance hydrogen production. Including biogas production in this quadrant indicates that researchers are likely exploring the simultaneous production of hydrogen and biogas, potentially aiming to maximize energy recovery from the fermentation process. The organic loading rate's position as a motor theme highlights the importance of process optimization in improving hydrogen yields. The niche themes quadrant contains more specialized and highly developed topics, including "adm1″, "mathematical modeling," "modelling," "biogas upgrading," "direct interspecies electron transfer," and "ammonia inhibition." These themes represent areas of intense research activity but with potentially limited scope or application. The presence of modeling-related terms suggests a strong emphasis on developing predictive tools and understanding the underlying mechanisms of dark photo fermentation. The inclusion of biogas upgrading indicates ongoing efforts to improve the quality and utility of the produced gases. Direct interspecies electron transfer and ammonia inhibition represent specific challenges or phenomena being studied to enhance the efficiency of the fermentation process. The emerging or declining themes quadrant is empty in this map, indicating either a lack of new emerging topics or that the field has reached a certain level of maturity where major new themes are not currently developing. This observation suggests that current research efforts focus on refining and optimizing existing concepts rather than exploring new directions. Based on these results, several areas for future research can be highlighted: (1) Integration of advanced modeling techniques with experimental studies to better predict and optimize hydrogen production; (2) Further investigation into the synergies between hydrogen and biogas production, potentially leading to more efficient co-production systems; (3) Development of strategies to mitigate ammonia inhibition and enhance direct interspecies electron transfer, thereby improving overall process efficiency; (4) Exploration of novel substrates or substrate combinations for anaerobic co-digestion to maximize hydrogen yields; (5) Research into scaling up niche technologies and concepts for practical, large-scale application; (6) Investigation of potential emerging themes that could revolutionize the field, such as the integration of dark photo fermentation with other renewable energy technologies or the application of synthetic biology to enhance hydrogen-producing microorganisms.

The factorial analysis in Fig. 13 presents a complex area of interconnected themes and processes. The plot is divided into two main clusters: a red cluster on the left and a blue cluster on the right. This

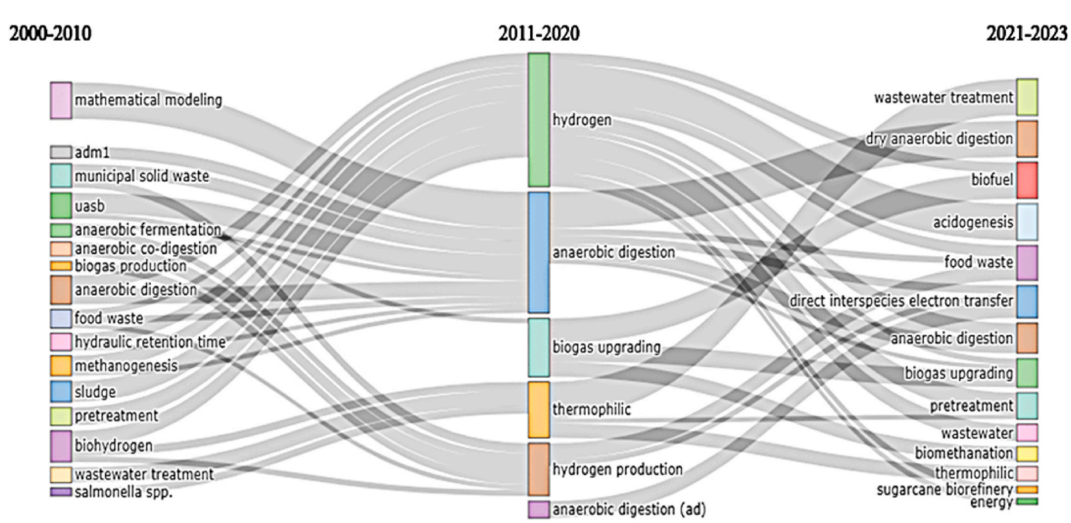

Fig. 11. Thematic evolution of keywords.

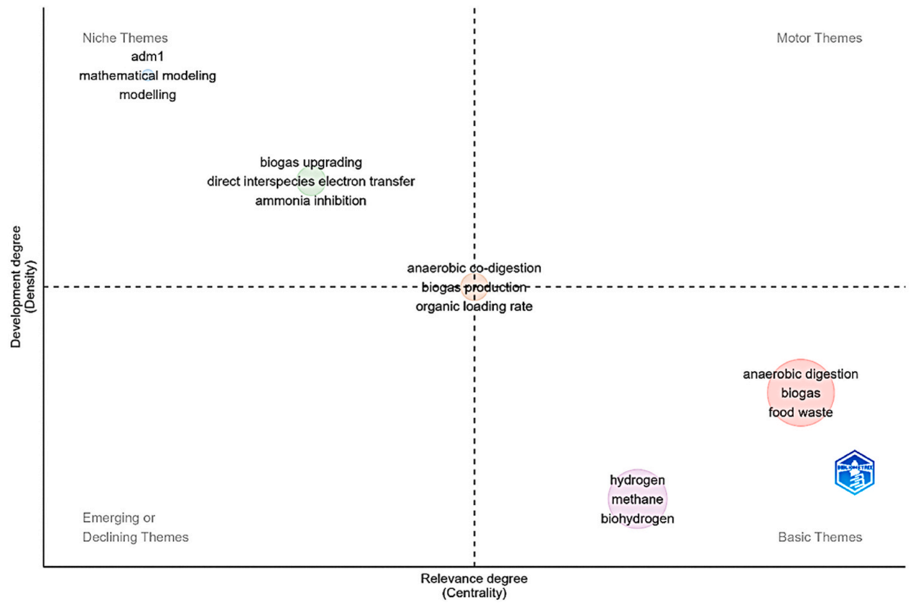

Fig. 12. Thematic map, author keywords (200 words).

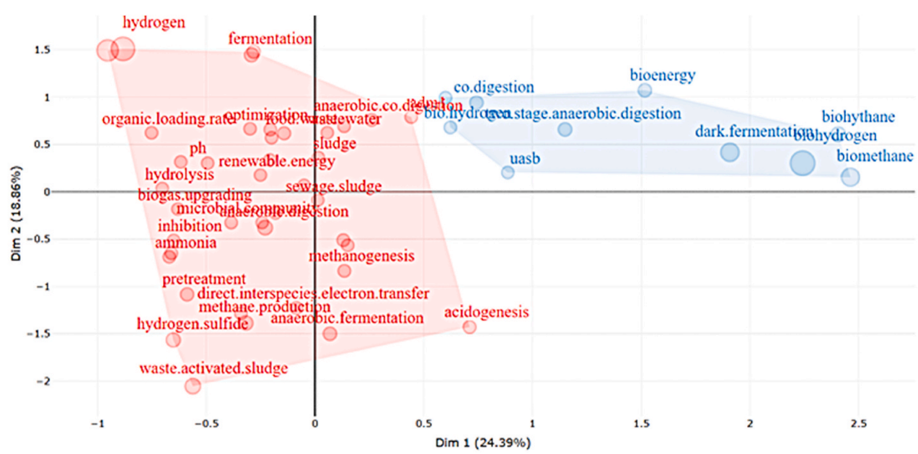

Fig. 13. Factorial analysis of author keywords.

indicates two distinct but related research focus areas. The red cluster comprises a wide range of topics related to the operational aspects and challenges of hydrogen production, including "organic loading rate," "optimization," "pH," "hydrolysis," "biogas upgrading," "inhibition," "ammonia," "pretreatment," and "direct interspecies electron transfer." This cluster highlights the importance of process optimization, addressing inhibitory factors, and enhancing substrate utilization for efficient hydrogen production. The presence of "renewable energy" in this cluster accentuates the broader context of sustainable energy production.

On the other hand, the blue cluster on the right side seems to focus more on the biological and technological aspects of the process, featuring terms like "bioenergy," "co-digestion," "two-stage anaerobic digestion," "dark fermentation," "biohydrogen," and "biomethane." This cluster suggests a research emphasis on integrated approaches to bioenergy production, potentially combining hydrogen production with other anaerobic processes for enhanced energy recovery. The positioning of "hydrogen" and "fermentation" at the top of the plot, straddling both clusters, indicates their central importance to the entire field of study. The vertical axis (Dim 2) appears to represent a spectrum from operational challenges (bottom) to product outcomes (top). In contrast, the horizontal axis (Dim 1) might represent a progression from process-focused research (left) to product-focused study (right). This layout implies that researchers are working on a continuum from addressing fundamental process challenges to developing integrated bioenergy systems.

These findings have important ramifications for how hydrogen produced by dark and photo fermentation will develop in the future. They suggest that while considerable focus is still on optimizing the core process and overcoming inhibitory factors, there is also a strong push towards integrating hydrogen production into broader bioenergy systems. "co-digestion" and "two-stage anaerobic digestion" indicate a trend towards more complex, multi-step processes that could improve overall energy yields. The emphasis on "waste activated sludge" and "wastewater" in the red cluster highlights the potential for combining the generation of energy with waste treatment, simultaneously addressing two critical environmental challenges. Furthermore, the prominence of "biogas upgrading" suggests ongoing efforts to improve the quality and usability of the gaseous products. The analysis also reveals the complex nature of research in this field, encompassing microbiology (e.g., "methanogenesis," "acidogenesis"), chemical engineering (e.g., "pH," "hydrolysis"), and environmental technology (e.g., "UASB").

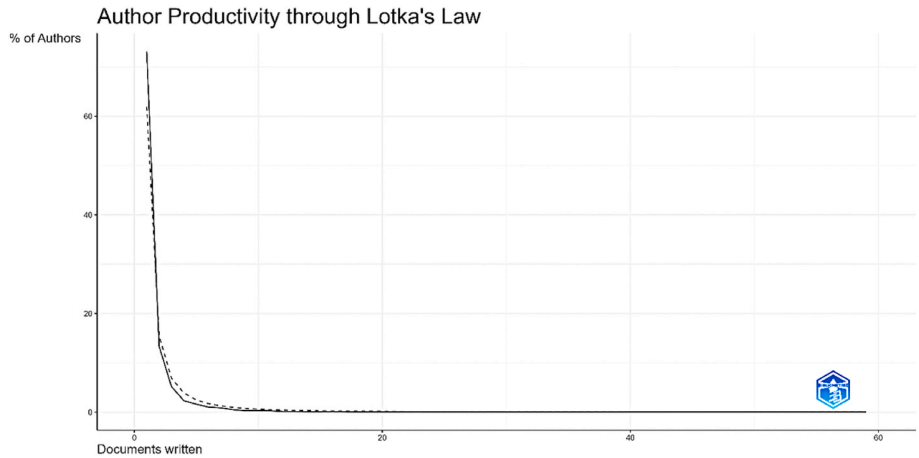

Fig. 14. Author productivity using Lotka's law.

4.5. Authors' productivity, citations, journals, and affiliations

Based on Lotka's law, the authors' productivity is shown in Fig. 14. This bibliometric analysis shows a highly skewed distribution of publications among authors, which is characteristic of many scientific fields. The y-axis represents the percentage of authors, while the x-axis shows the number of documents written. The curve demonstrates a sharp decline, indicating that a small proportion of authors are responsible for many publications. At the same time, most researchers publish only one or a few papers on this topic. This pattern aligns with Lotka's law, which posits that the number of authors making n contributions is approximately $1/n^2$ of those making one contribution, with the frequency decreasing as the number of contributions increases [88,89]. In the context of hydrogen production via dark photo fermentation, this distribution suggests a field dominated by a core group of highly productive researchers, likely experts or established teams, surrounded by a larger periphery of occasional contributors. Such a structure has several implications for the field. For example, it may indicate a concentration of expertise and resources in select institutions or research groups, potentially leading to rapid advancements and risking a narrow focus in research directions. Many single-publication authors could represent new entrants to the field, interdisciplinary contributions, or researchers who have shifted their focus elsewhere after initial exploration. This dynamic may bring fresh perspectives but also suggest challenges in sustaining long-term research programs in this area. For the scientific community, this distribution highlights the importance of collaboration and knowledge sharing to broaden the base of expertise and foster innovation.

Table 1 shows the top 30 most relevant cited papers. It can be seen that studies on hydrogen production through dark fermentation have demonstrated significant progress and potential as a sustainable energy source. The studies presented in Table 1 highlight various aspects of this technology, including substrate utilization, operational parameters, microbial communities, and process optimization. One of the most cited papers by Liu et al. [90] showed the feasibility of hydrogen production from acetate through a microbial fuel cell (MFC) system. This breakthrough showed that hydrogen could be produced directly from oxidized organic matter efficiently by augmenting the electrochemical potential with an additional voltage. This finding is particularly significant as it overcomes the limitations of traditional fermentation processes, which are typically restricted to carbohydrate substrates. Utilizing any biodegradable dissolved organic matter for hydrogen production creates new opportunities for waste management and energy generation.

Some papers focused on optimizing fermentation using various substrates and operational conditions. Hawkes [91] and Hawkes et al. [92] emphasized the importance of using stable mixed cultures enriched from natural sources, such as heat-treated sewage sludge, for practical applications. These mixed cultures can function effectively with non-sterile feedstocks, enhancing the economic viability of the process. The study emphasized the importance of process parameters, including temperature, pH, and hydraulic retention time (HRT), in optimizing hydrogen yield. According to their study, phosphate, a complex nitrogen source, can be used to optimize feedstock that is rich in carbohydrates. Guo et al. [93] looked at three types of agricultural residue: food waste, animal manure, and waste directly produced from agriculture. Each of the three can serve as a substrate for dark fermentation, which produces hydrogen. More investigation is necessary to grasp how substrate composition affects biohydrogen performances fully. The results show that the biological processes are susceptible to operating conditions, including high temperature, low partial pressure, low pH, and acclimated microbial communities. To convert biodegradable organic matter into bioenergy, it was suggested to combine a hydrogen fermentor with a methanogenic reactor. In addition, the study proposes the distinction of three classes of microorganisms: metabolic competitors, hydrogen consumers, and producers of hydrogen; these classes need to be further characterized in mixed cultures.

The impact of operational parameters on hydrogen production emerged as a consistent theme across several studies. For example, Mizuno et al. [94] investigated how nitrogen sparging affected the amount of hydrogen produced in a mixed culture enriched with soy meal. The reactor was run using a glucose-mineral salts medium at 35 °C and pH 6.0. Following eight weeks of nonstop operation, the culture yielded consistent amounts of hydrogen. Following 5 h of rest, the hydrogen yield was 53.4% H_2 and 0.85 mol H_2/mole of glucose. A nitrogen sparging flow rate fifteen times higher than the hydrogen production rate achieved a hydrogen yield of 1.43 mol of H_2 per mole of glucose consumed. Under these sparging conditions, the specific hydrogen production rate increased from 1.446 ml of hydrogen per minute per gram of biomass to 3.131 ml. The study highlighted that a significant factor affecting hydrogen yield is the partial pressure of hydrogen in the liquid phase. This finding has important implications for process design and optimization. Mesophilic and thermophilic acidogenic cultures that were acclimated to food waste at 5 days HRT were used by Ref. [95] to evaluate the production of hydrogen from food waste. In contrast to the mesophilic acidogenic culture, which contained methane, the thermophilic acidogenic culture generated biogas devoid of methane at all pH and VS concentrations tested. Owing to methane-free conditions and minimal propionate production, the thermophilic acidogenic culture generated a notably higher amount of hydrogen than the mesophilic culture. With a maximum hydrogen content of 69% at a volatile solids (VS) concentration of 10 g VS L^{-1}, higher VS concentrations enhanced both the quantity and quality of

Table 1
Top 30 most relevant cited papers.

Author(s)	Title of paper	Total citations	Total citations per Year
Liu et al. [90]	"Electrochemically Assisted Microbial Production of Hydrogen from Acetate"	911	45.55
Hawkes [91]	"Sustainable fermentative hydrogen production: challenges for process optimization"	845	36.74
Guo et al. [93]	"Hydrogen production from agricultural waste by dark fermentation: A review"	686	45.73
Hawkes et al. [92]	"Continuous dark fermentative hydrogen production by mesophilic microflora: Principles and progress"	612	34.00
Mizuno et al. [94]	"Enhancement of hydrogen production from glucose by nitrogen gas sparging"	517	20.68
Shin [95]	"Hydrogen production from food waste in anaerobic mesophilic and thermophilic acidogenesis"	406	19.33
Kim [96]	"Feasibility of biohydrogen production by anaerobic co-digestion of food waste and sewage sludge"	389	18.52
Antonopoulou et al. [97]	"Biofuels generation from sweet sorghum: Fermentative hydrogen production and anaerobic digestion of the remaining biomass"	385	22.65
Steinbusch et al. [114]	"Biological formation of caproate and caprylate from acetate: fuel and chemical production from low grade biomass"	369	26.36
Ren et al. [98]	"Biohydrogen production from molasses by anaerobic fermentation with a pilot-scale bioreactor system"	369	19.42
Chen et al. [99]	"Fermentative hydrogen production with Clostridium butyricum CGS5 isolated from anaerobic sewage sludge"	346	17.30
Lin [100]	"Carbon/nitrogen-ratio effect on fermentative hydrogen production by mixed microflora"	337	16.05
Chang [101]	"Biohydrogen production using an up-flow anaerobic sludge blanket reactor"	330	15.71
Luo & Angelidaki [102]	"Integrated biogas upgrading and hydrogen utilization in an anaerobic reactor containing enriched hydrogenotrophic methanogenic culture"	274	21.08
Zhao et al. [115]	"Towards engineering application: Potential mechanism for enhancing anaerobic digestion of complex organic waste with different types of conductive materials"	266	33.25
Yang et al. [116]	"Adding granular activated carbon into anaerobic sludge digestion to promote methane production and sludge decomposition"	265	33.13
Hori et al. [103]	"Dynamic transition of a methanogenic population in response to the concentration of volatile fatty acids in a thermophilic anaerobic digester"	263	13.84
Chen et al. [117]	"Kinetic study of biological hydrogen production by anaerobic fermentation"	257	13.53
Mus et al. [118]	"Anaerobic Acclimation in Chlamydomonas reinhardtii: Anoxic Gene Expression, Hydrogenase Induction, and Metabolic Pathways"	256	14.22
Lim et al. [119]	"Anaerobic organic acid production of food waste in once-a-day feeding and drawing-off bioreactor"	252	14.82
Mohan et al. [104]	"Anaerobic biohydrogen production from dairy wastewater treatment in sequencing batch reactor (AnSBR): Effect of organic loading rate"	247	13.72
Wang et al. [105]	"Producing hydrogen from wastewater sludge by Clostridium bifermentans"	246	11.18
Valdez-Vazquez [106]	"Semi-continuous solid substrate anaerobic reactors for H_2 production from organic waste: Mesophilic versus thermophilic regime"	229	11.45
Venetsaneas [107]	"Using cheese whey for hydrogen and methane generation in a two-stage continuous process with alternative pH controlling approaches"	227	14.19
Chen et al. [108]	"Biohydrogen production using sequential two-stage dark and photo fermentation processes"	226	13.29
Yang et al. [109]	"Biohydrogen production from cheese processing wastewater by anaerobic fermentation using mixed microbial communities"	217	12.06
Lin and Lay [110]	"Effects of carbonate and phosphate concentrations on hydrogen production using anaerobic sewage sludge microflora"	210	10.00
Luo et al. [111]	"Enhancement of bioenergy production from organic wastes by two-stage anaerobic hydrogen and methane production process"	201	14.36
Safari and Dincer [112]	"Development and analysis of a novel biomass-based integrated system for multigeneration with hydrogen production"	182	30.33
Zhu et al. [113]	"Co-production of hydrogen and methane from potato waste using a two-stage anaerobic digestion process"	176	10.35

hydrogen production. The hydrogen yield peaked at 6 g VS L^{-1}, ranging from 0.9 to 1.8 mol-H_2/mol-hexose. According to a study by Ref. [96], the anaerobic co-digestion of sewage sludge and food waste can effectively produce hydrogen. As the sewage sludge composition increased to 13–19% across all VS concentrations, food waste's specific hydrogen production potential increased relative to sewage sludge. The optimal waste composition of 87:13 (food waste to sewage sludge) at a VS concentration of 3.0% demonstrated the highest hydrogen production potential. Additionally, hydrogen production potential was positively correlated with protein and carbohydrate concentrations, suggesting that enriching the substrate with protein could further enhance hydrogen yields. The study concluded that both sewage sludge and food waste are suitable primary and secondary substrates for hydrogen production. In addition, several researchers investigated using specific substrates for hydrogen production. The use of biomass from sweet sorghum as a source of methane and hydrogen was examined in the study conducted by Ref. [97]. Methane production from the hydrogenogenic process and leftover solids was evaluated, and hydrogen production from sugar fermentation was tested at different HRTs. At 6

HRT, the highest hydrogen production rate (2550 ml H_2/d) was attained, and at 12 HRT, the highest hydrogen yield (10.4 l H_2/kg sweet sorghum) per kg of sorghum biomass was attained. With about 29 l CH_4/kg of sweet sorghum, the hydrogenogenic reactor's effluent was a perfect substrate for methane production. The anaerobic digestion of solid residues produced 78 l of CH_4/kg of sweet sorghum. This two-stage process highlights the potential for maximizing energy recovery from biomass. Ren et al. [98] conducted a 200-day pilot study on biohydrogen production using a continuous flow anaerobic fermentation reactor, with molasses as the substrate. The hydrogen bio-producing reactor (HBR) operated at organic loading rates (OLR) ranging from 3.11 to 85.57 kg COD/m^3 reactor/day (where COD refers to chemical oxygen demand). The yields of hydrogen and biogas increased with OLR but declined at higher loading rates. The main components of the biogas were CO_2 and H_2, with hydrogen comprising between 40% and 52% of the total volume. A specific hydrogen production rate of 0.75 m^3 H_2/kg mlVSS/day was recorded, achieving a maximum hydrogen production rate of 5.57 m^3 H_2/m^3 reactor/day and a 26.13 mol/kg COD hydrogen yield. The hydrogen yield was influenced by the concentrations of ethanol and acetate in the liquid phase. Additionally, the microbial aspects of dark fermentation were also extensively examined. Chen et al. [99] investigated the hydrogen production capacity of a *Clostridium butyricum* strain, specifically *C. butyricum CGS5*, using a sucrose-based medium under various conditions. Isolated from sewage sludge, this strain demonstrated efficient growth and hydrogen production in an iron-containing medium. The optimal hydrogen production and yield were achieved at a pH of 5.5 with an initial sucrose concentration of 20 g COD/L (17.8 g/L). Notably, the CGS5 strain exhibited its highest hydrogen production rate at a medium pH of 6.0. While it grew more rapidly and produced more hydrogen at pH levels of 6.0 and 6.5, this swift carbon source conversion into biomass reduced yield. Additionally, when cultured at a pH of 5.0, the strain did not produce hydrogen and showed no signs of growth. Their findings regarding optimal pH, sucrose concentration, and medium composition enhance the understanding of creating ideal conditions for hydrogen-producing microorganisms. Furthermore, [100], conducted a batch experiment to investigate the impact of the carbon/nitrogen (C/N) ratio on biological hydrogen production from sucrose using anaerobic sewage sludge that had been acclimated to sugar. Based on the findings, anaerobic microorganisms in sewage sludge's capacity to produce hydrogen was strongly influenced by the inorganic C/N ratio. The production rate and productivity of hydrogen rose by 80% and 500%, respectively, at a C/N ratio of 47 when compared to the control. This underscores the critical role of nutrient balance in optimizing the fermentation process.

Developing reactor designs for hydrogen production was another critical area of research. In the [101] study, an up-flow anaerobic sludge blanket (UASB) reactor produced hydrogen gas through sewage sludge to establish enrichment cultures that produce hydrogen. It was discovered that the system was appropriate for producing hydrogen, with hydraulic retention times of 24-4 h. Hydrogen productivity depended on HRT and was almost constant between 8 and 20 h, but it dropped after 4 or 24 h. Following an 8-h peak, the hydrogen and specific hydrogen production rates (HPR) decline at all other HRTs. Acetate and butyrate were the principal volatile fatty acids of fermentation. The kinetic constants for the anaerobic granule sludge were yield coemean cell retention time, excess sludge discharge rate, and endogenous decay. Their work contributes to understanding how reactor design and operation can be optimized for hydrogen production. Other studies also explored the integration of hydrogen production with different processes. In view of this, a novel technique for upgrading biogas in a separate biogas reactor fed with hydrogen and biogas and enriched with hydrogenotrophic methanogens was presented in the study by Ref. [102]. Hydrogen was added to both thermophilic and mesophilic anaerobic cultures to enhance the conversion of CO_2 to CH_4. A bioconversion rate of 320 ml CH_4/(gVSS) h was obtained by enrichment at 55 °C, which is more than 60% higher than at mesophilic temperatures. In mesophilic and thermophilic enriched cultures, various dominant species were detected. These species are all members of the *Methanobacteriales* order and can mediate hydrogenotrophic methanogenesis. After the biogas upgrading was tested in various settings, the generated biogas had a steady-state CH_4 content of about 95%. The investigation also demonstrated that raising stirring speed and reducing gas-liquid mass transfer led to an approximate 95% increase in CH_4 content. This innovative approach demonstrates how hydrogen can enhance biogas' quality, potentially increasing its value and applications.

Similarly, some researchers also delved into microbial community dynamics during hydrogen production. For instance, an investigation by Ref. [103] looked at the microbial communities' succession under acidification and neutralization conditions in a thermophilic methanogenic bioreactor. It was discovered that the bacterial population was affected by pH, but the archaeal community structure was closely correlated with the concentration of VFAs. *Methanosarcina* sp., an aceticlastic methanogen, and *Methanoculleus* sp., two species of hydrogenotrophic methanogen, made up the archaeal community. According to quantitative PCR, Methanoculleus sp. was the predominant methanogen under stable conditions. Methanothermobacter sp.'s 16S rRNA gene was dramatically overexpressed due to the dynamic transition of hydrogenotrophic methanogens brought about by the accumulation of VFAs. The dominance of one species gave way to the other in response to the concentration of VFA, indicating that the concentration of dissolved hydrogen was a deciding factor. In the thermophilic anaerobic digester, the simple methanogenic population responded strongly to the surrounding conditions, particularly the concentration of VFAs. Their findings on how changes in VFA concentration and pH affect archaeal and bacterial communities provide valuable insights into the complex microbial ecology of these systems.

Furthermore, [104], assessed the use of pretreated mixed consortia in a suspended growth sequencing batch reactor (AnSBR) to produce biological hydrogen (H_2) from dairy wastewater. The bioreactor was run for 24 h at mesophilic and acidophilic temperatures. The substrate/OLR of the wastewater utilized greatly affected the rate of H_2 evolution. Both H_2 generation and COD reduction indicated a tendency toward rapid stabilization in system. A spike in pH values was noticed during the stabilized phase of operation. With H_2 generation taking 39 days, 3.5 days, and 4.7 days, respectively, the system demonstrated a tendency toward rapid stabilization. For a full 24-h cycle, the bioreactor was run at mesophilic conditions. The reactor operating conditions (acidophilic pH 6) are optimal for effective H_2 yield. The system integrates suspended configuration with sequencing/periodic discontinuous batch operation, offering flexibility and cost efficiency. It is a practical, cost-effective, and promising approach for large-scale H_2 production and wastewater treatment. Another research by Ref. [105] used a clostridium strain as an inoculum to explore the bio-conversion of wastewater sludge to hydrogen. A higher yield of hydrogen was observed in the results.

Additionally, the study looked at how five pre-treatments-ultrasonication, acidification, sterilization, freezing/thawing, and addition of methanogenic inhibitor—affect hydrogen production. In comparison to untreated sludge, the specific hydrogen yield rose by 1.5–2.5 times after freezing, thawing, and sterilizing; in contrast, the specific hydrogen yield decreased after adding an inhibitor and ultrasonication. An investigation by Ref. [106] looked at how operation temperature affected organic municipal solid waste semicontinuous acidogenic solid substrate anaerobic digestion (A-SSAD). The results indicated that the H_2 percentage for the thermophilic regime was higher than that of the mesophilic regime (58% versus 42%, respectively). The maximum yield of A-SSAD was 37% for mesophilic A-SSAD and 80% for thermophilic A-SSAD. The study also discovered that mesophilic A-SSAD spent solids had higher concentrations of butyrate, whereas thermophilic A-SSAD digestates had higher concentrations of acetic acid. Contrary to earlier reports that suggested batch and semicontinuous processes were less efficient, the semicontinuous process produced moderate-to-high yields.

In a two-stage continuous process, the use of cheese whey as a source of hydrogen and methane was also examined in the [107] study. An automated pH controller or the addition of alkalinity was employed to maintain a consistent pH throughout the 24-h hydraulic retention time (HRT) during mesophilic fermentative hydrogen production from undiluted cheese whey. The process achieved a hydrogen yield of approximately 0.78 ± 0.05 mol H_2 per mole of glucose consumed, with a hydrogen production rate of 2.9 ± 0.2 L/L reactor/day. The corresponding hydrogen yields were 2.9 L of H_2/L of cheese whey and 1.9 L of H_2/L of cheese whey. Subsequently, the wastewater underwent additional digestion in a continuously operated mesophilic anaerobic bioreactor, producing biogas with a yield of 6.7 L of CH_4/L of influent, equivalent to about 1 L of CH_4/day. In a study by Ref. [108], a two-stage process that combined dark and photo fermentation was employed to reduce chemical oxygen demand (COD) in effluent while increasing hydrogen yield from sucrose. The dark-H_2 fermentation phase utilized Clostridium pasteurianum CH_4, which produced 3.80 mol H_2 per mole of sucrose. In the subsequent photo fermentation stage, soluble metabolites from the dark fermentation, such as butyric and acetic acids, were used to generate hydrogen. The phototrophic bacterium *Rhodopseudomonas palustris* WP3-5 achieved a total hydrogen yield of 10.02 mol H_2 per mole of sucrose. Overall, the process resulted in a 72.0% reduction in COD. With the addition of side-light optical fiber illumination and 2.0% (w/v) clay carrier, the total hydrogen yield increased to 14.2 mol H2 per mole of sucrose, achieving nearly 90% COD removal. The study by Ref. [109] examined the anaerobic fermentation of mixed microbial communities in mesophilic environments to produce hydrogen from wastewater from cheese processing. In batch H_2 fermentation experiments, H_2 yields of 8 and 10 mM/g COD fed at 1.0 and 1.5 food-to-microorganism ratios were obtained, respectively. Valeric, propionic, acetic, and butyric acids were the main volatile fatty acids generated. A completely mixed reactor (CSTR) was used for the continuous H_2 fermentation experiments, and carbonate was added to the feed material to regulate pH. Maximum H_2 yields for loading rates (LRs) tested with a 24-h HRT ranged from 1.8 to 2.3 mM/g COD fed. According to the 16S rDNA analysis, approximately 5% of the bacteria were *Clostridia,* and more than 50% of the bacteria were *Lactobacillus*. Concurrent declines in the genus *Lactobacillus* were noted, with a decrease in H_2 production.

Finally, anaerobic sewage sludge acclimated to sucrose was used in a batch experiment by Ref. [110] to examine the effects of phosphate and carbonate on biological hydrogen production. They carried out a concentration experiment using the Taguchi orthogonal array. The findings demonstrated that NH_4HCO_3, Na_2HPO_4, and Na_2CO_3 impacted the anaerobic microorganisms' capacity to produce hydrogen in sewage sludge, with Na_2HPO_4 being the most important supplement. Compared to an acidogenic nutrient formulation, the hydrogen production was 1.9 times higher at the ideal 600 mg/L Na_2HPO_4 concentration. According to the study, phosphate addition as a building capacity supplement may be beneficial for the best possible hydrogen production operations using anaerobic sewage cultures instead of carbonate addition. The research by Ref. [111] investigated the possibility of producing more bioenergy from organic wastes through a two-stage anaerobic hydrogen and methane process. A single-stage methanogenic process under 3 gVS/(L d) organic loading produced 11% less energy than the two-stage process with hydraulic retention times of 3 and 12 days. As the organic loading rate was increased to 4.5 gVS/(L d), the process stayed stable, but the single-stage process did not work. Additionally, the study discovered that increasing the $HRT_{hydrogen}$: $HRT_{methane}$ ratio from 3:12 to 1:14 can boost energy output. Safari and Dincer [112] looked into the energy and exergy evaluation of a multi-generation integrated system that utilizes the anaerobic digestion of sewage sludge from a wastewater treatment plant (WWTP). Along with heat recoveries for increased efficiency, the system produced power, freshwater, heat, and hydrogen. The system produced power through an open-air Brayton cycle, an organic Rankine cycle, and desalination with waste heat to purify water. Hydrogen was produced electrochemically using a proton exchange membrane (PEM) electrolyzer. The heat rejected from the ORC's working fluid was used in the heating process. In that order, the electricity, hydrogen, freshwater, and hot water output rates were 1.82 kg/s, 0.347 kg/h, 0.94 kg/s, and 1102 kW. The overall energy and energy efficiencies are 63.6% and 40%, respectively. Zhu et al. [113] investigated the co-production of hydrogen and methane through anaerobic digestion of potato waste. The methane production phase was conducted in both continuous and semi-continuous flow systems, with hydraulic retention times (HRTs) of 30 and 90 h, respectively. Meanwhile, the hydrogen production phase operated continuously at a pH of 5.5 and an HRT of 6 h. Over a 110-day period, the hydrogen stage achieved a maximum gas production rate of 270 ml/h, with an average rate of 119 ml/h and a hydrogen concentration of 45%. In the methane reactor, the average methane concentration reached 76%, yielding production rates of 187 ml/h and 141 ml/h. The study reported a reduction of 64% in the total chemical oxygen demand (COD) of the feedstock and a 70% reduction in its volatile solids. The overall energy yield was determined to be 2.14 kWh/kg of total solids.

Producing hydrogen from various organic substrates, including waste materials, offers a sustainable solution to waste management and clean energy production. The optimization of process parameters and reactor designs brings us closer to commercially viable hydrogen production through dark fermentation. Understanding microbial community dynamics and the role of specific microorganisms in hydrogen production provides a foundation for developing more efficient and stable processes. The integration of hydrogen production with other processes, such as biogas upgrading, demonstrates the potential for creating more comprehensive and efficient energy systems. However, challenges remain, including scaling up the technology, improving efficiency, and addressing potential inhibition factors. Future research should focus on overcoming these challenges and further optimizing the process for industrial-scale applications. As we seek sustainable alternatives to fossil fuels, hydrogen production through dark fermentation represents a promising avenue for clean energy production, waste valorization, and environmental protection.

The total citations for the top 20 most cited countries are displayed in Fig. 15. It can be seen that China tops with 28,123 citations, more than triple the citations of the next highest country. This dominant position suggests that China is at the forefront of research in this area, potentially driving significant advancements and innovations in hydrogen production technology. The United States follows with 8280 citations, indicating a strong but considerably lower impact than China. India secures the third position with 5125 citations, indicating its growing influence in this research domain. Denmark ranks fourth with 4746 citations. The presence of diverse countries from Europe (United Kingdom, Italy, France, Spain, Germany, Greece, Sweden, Netherlands), Asia (Korea, Japan, Thailand, Malaysia), North America (USA, Canada, Mexico), South America (Brazil), and Oceania (Australia) in the top 20 highlights the global nature of this research area. This worldwide engagement implies the universal recognition of hydrogen's potential as a clean energy source and the importance of developing efficient production methods. The distribution of citations among these countries implies varying levels of research output, quality, and international collaboration. Countries with higher citation counts will likely produce more influential research, potentially due to advanced research facilities, substantial funding, or collaborative solid networks. The results demonstrate that knowledge and expertise in hydrogen production through dark photo fermentation are concentrated in specific countries, which could lead to technological advantages and potential leadership in future energy markets. The significant gap between China and other countries suggests a possible shift in the global balance of scientific influence in this field.

Furthermore, the presence of developed and developing nations in

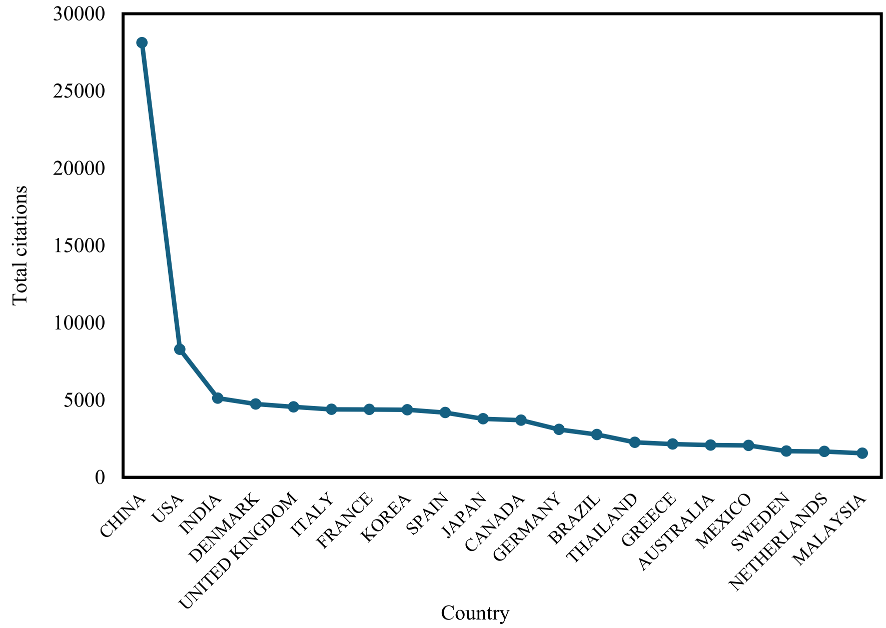

Fig. 15. Top 20 most cited countries.

the list points to the widespread recognition of hydrogen's importance in future energy strategies. For countries with lower citation counts, there may be opportunities to strengthen their research capabilities and international collaborations to enhance their impact. The diverse geographical representation also suggests that different climates, resources, and technological contexts are being considered in the research, which is crucial for developing globally applicable solutions. However, the absence of African countries and the limited representation from certain regions highlight potential gaps in global research participation that may need addressing to ensure the comprehensive development of this technology.

The most relevant affiliations are shown in Fig. 16, with the Technical University of Denmark leading with 174 articles, Tongji University with 163 articles, and Hunan University with 152 articles. This result shows a substantial concentration of research efforts in this field, predominantly in Chinese institutions, with eight out of the top ten affiliations being Chinese universities or research centers. The strong presence of Chinese institutions, including Zhejiang University, Jiangnan University, and Beijing Institutions, emphasizes China's significant investment and focus on alternative energy research, particularly in hydrogen production technologies. The high number of publications from these institutions suggests a robust and sustained research program in dark photo fermentation, indicating its perceived potential as a viable method for hydrogen production. The presence of the Technical University of Denmark at the top of the list is noteworthy, highlighting Europe's involvement in this research area and suggesting possible international collaborations or competitive research initiatives. The University of Tsukuba's inclusion adds a Japanese perspective to the research area, further emphasizing the global interest in this technology. The concentration of research in academic institutions implies a strong

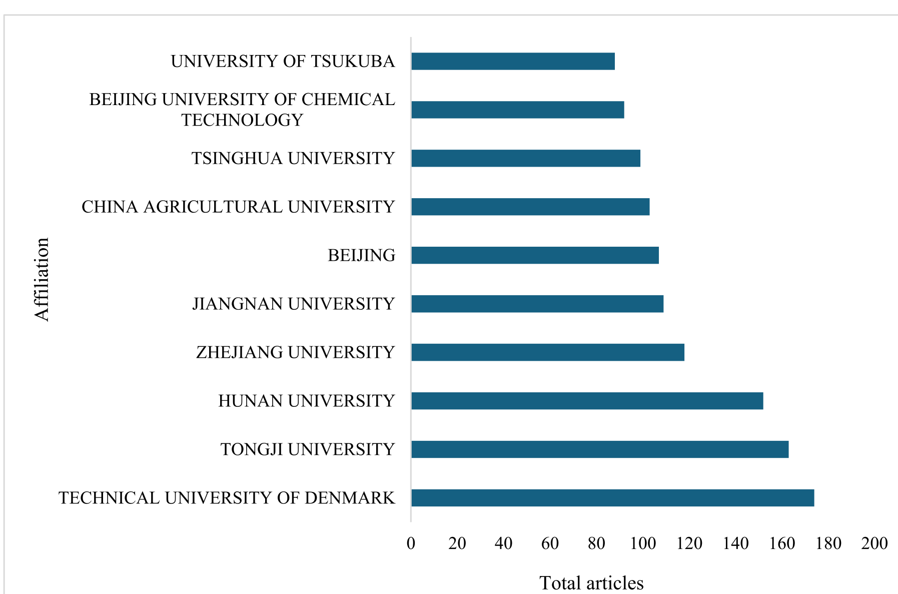

Fig. 16. Most relevant affiliations.

focus on fundamental and applied research in dark photo fermentation, potentially driving innovations in biohydrogen production techniques. This research intensity could lead to significant advancements in the efficiency and scalability of hydrogen production through dark photo fermentation, potentially positioning it as a critical technology in the transition towards a hydrogen-based economy.

Fig. 17 illustrates the most prominent journals within the study period. Bioresource Technology emerges as the leader with 643 articles, significantly outstripping other journals and establishing itself as the primary platform for disseminating research in this area. The International Journal of Hydrogen Energy follows with 256 articles, reinforcing its importance in the hydrogen energy sector. Water Research ranks third with 125 articles, pinpointing the interconnection between water management and hydrogen production through dark photo fermentation. The presence of Chemosphere and Renewable Energy indicates this research's environmental and sustainable energy aspects. The Journal of Cleaner Production and Environmental Science and Technology further emphasizes dark photo fermentation studies' environmental implications and sustainability focus. The appearance of Energies and Energy Conversion and Management highlights the broader energy sector's interest in this technology. The Chemical Engineering Journal's presence suggests the critical role of chemical engineering principles in advancing dark photo fermentation techniques. This distribution of publications across various journals reveals the multidisciplinary nature of dark photo fermentation research, comprising fields such as biotechnology, environmental science, energy engineering, and chemical engineering. The dominance of Bioresource Technology suggests that much of the current study is focused on the biological and technological aspects of the process, potentially emphasizing the optimization of microbial strains, reactor designs, and substrate utilization. The strong representation of hydrogen-specific and energy-focused journals indicates the technology's perceived potential as a significant contributor to future clean energy systems. The addition of water-related and environmental journals points to the technology's relevance in addressing water treatment challenges while simultaneously producing clean energy, highlighting its potential for dual benefits in environmental management.

4.6. The three-field plot

The three-field plot presented in Fig. 18 shows a comprehensive visualization of the research areas in keywords (left), university affiliations (middle), and countries (right). The figure reveals a complex network of relationships between these three elements, providing insights into the global distribution of research efforts and focus areas. On the left side, show various keywords, with "waste-activated sludge" appearing as a prominent area of study, followed by other words such as "hydrogen sulfide," "fermentation," and "anaerobic digestion." These topics strongly emphasize utilizing waste materials and biological processes for hydrogen production. The central column (middle) lists numerous universities and research institutions, with Hunan University, Technical University of Denmark, Tongji University, and Zhejiang University among the top contributors. This indicates a mix of Chinese and European institutions leading the research efforts in this field. The right column shows the countries involved, with China dominating the research output, followed by Japan, Denmark, and several other nations, including Australia, Ireland, France, and Brazil. The dense network of connections between the three fields illustrates the complicated nature of the research, with many institutions working across multiple topics and international collaborations evident. The strong presence of Chinese institutions and the country's overall dominance in the field suggest that China is investing heavily in this area of renewable energy research. The involvement of institutions from various countries indicates the global interest in dark photo fermentation as a potential solution for sustainable hydrogen production. The diversity of research topics linked to multiple institutions and countries implies a comprehensive approach to tackling the challenges associated with this technology, from waste management to process optimization. These findings have important ramifications for waste management and renewable energy in the future. The focus on waste-activated sludge and other waste materials as substrates for hydrogen production through dark photo fermentation suggests a move towards more sustainable and circular economy approaches in energy production. The international nature of the research, albeit with a strong Chinese influence, may lead to faster advancements through knowledge sharing and collaborative efforts. However, it also raises questions about the potential for technological leadership and intellectual property rights in this emerging field. The involvement of institutions from developed and developing countries indicates the global recognition of hydrogen as a crucial component of future energy systems. This research focus could accelerate the development of economically viable and environmentally friendly hydrogen production methods, potentially revolutionizing the energy sector and bringing significant weight to global endeavors aimed at mitigating climate change and curbing carbon emissions.

4.7. Challenges and potential strategies to improve the various processes

Even though DF has several advantages, mostly demonstrated in lab

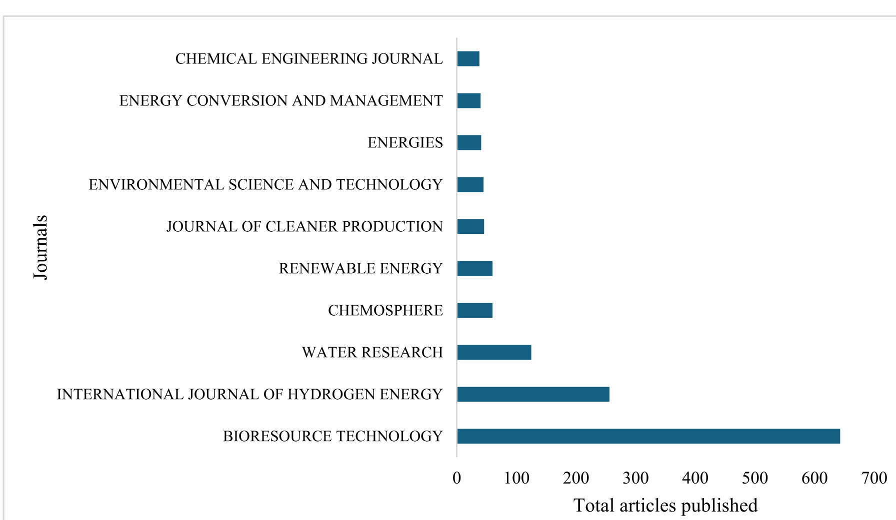

Fig. 17. Most relevant journals.

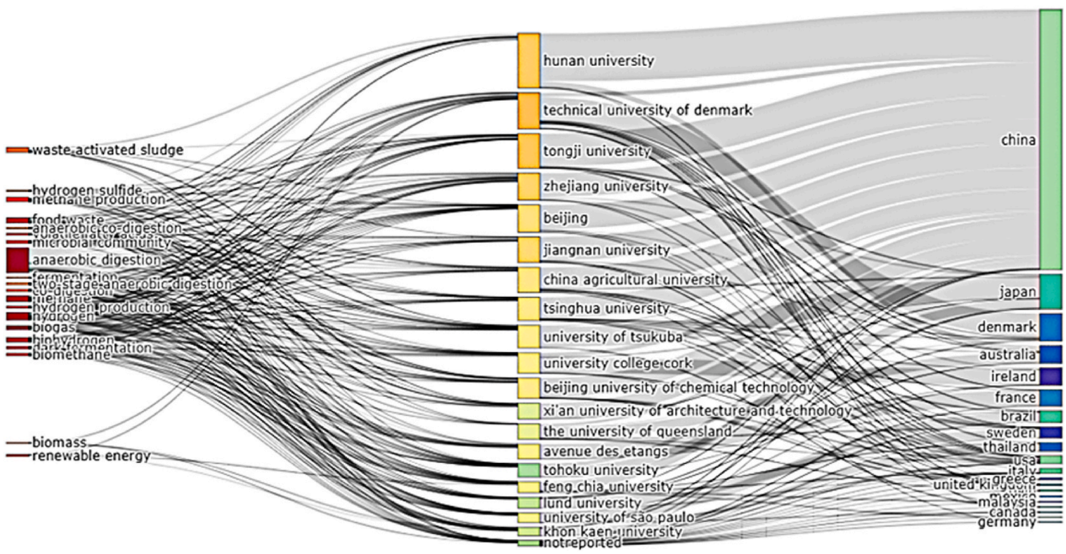

Fig. 18. Three field plots: left (keywords), middle (affiliations), and right (countries).

settings, such as a high rate of H_2 production, low energy input, ease of handling, and sustainability, further advancements in cost, efficiency, and dependability are still required to make this technology viable for use in commercial H2 production from organic waste [17]. Premature conversion of biohydrogen into undesirable products is a possibility, according to Ref. [120]. Methanogens that oxidize biohydrogen and reduce CO_2 into methane gas (CH_4) and acetate are the primary cause of the conversion. These organisms are also known as home-acetogens, or Methanobacteriales and Acetobacterium. Utilizing the dark fermentation process at a low pH could help to reduce these difficulties by potentially preventing the growth of home-acetogens and methanogens [120]. Selecting biohydrogen producers could be accomplished by suppressing reactions that consume biohydrogen through seed culture pre-treatment techniques like heat, sonification, acid/alkali treatment, and others [121]. A new route for the production of biohydrogen may also be opened up by the idea of combining wastewater or wastewater and solid organic wastes, according to Lin et al. [122] to reach a desired C/N ratio, various waste types could be mixed. When utilizing food waste along with primary sludge and waste-activated sludge as feedstocks, Zhu et al. [123] found that biohydrogen production increased compared to solely one type of waste. Nevertheless, the type of sludge used and the mixing ratio affect how co-digestion combinations work. As chemicals are not utilized as carbon or nitrogen sources to achieve the necessary C/N ratio, the suggested technique may also lower production costs [121].

Similarly, there are several challenges in biohydrogen production through photo fermentation. For example, photosynthetic bacteria have limited ability to absorb solar energy, which could result in a very low light transformation efficiency for biohydrogen production [124]. The right sterile environmental conditions are also necessary for these bacteria to grow and produce hydrogen. Furthermore, high energy demands are necessary for nitrogenase enzymes to carry out the photo-fermentation process because of the high activation energy. In addition, the cell shadowing effect lowers light intensity for lower performance in biohydrogen production by reducing light penetration inside the photoreactor. A sizable land coverage area is necessary to achieve an effective anaerobic photobioreactor for a large-scale application [59]. A metabolic switch from producing biohydrogen to synthesizing polyhydroxybutyrate (PHB) and an uneven light distribution has been identified as additional photo fermentation difficulties. Biohydrogen and PHB synthesis production share a reducing power that arises from the metabolism of organic acids, which puts them in competition [125]. Furthermore, the medium's nitrogen content may impact the nitrogenase enzyme. A high nitrogen content can inhibit nitrogenase synthesis and decrease biohydrogen generation. The waste materials' dark color may make it harder for light to penetrate. Several strategies are proposed to increase the yield of biohydrogen through photo fermentation. These include creating new strains of photosynthetic bacteria more resistant to ammonium concentration and VFA and developing new technologies for more efficient lighting and light distribution. Additionally, maintaining a minimal hydrogenase activity but a maximal nitrogenase activity, along with a favorable carbon-to-nitrogen source molar ratio, can increase biohydrogen yields [126]. Combining dark fermentation and photo fermentation in a hybrid system or two-stage process may increase a single substrate's production yield and conversion efficiency. During the second stage of photo fermentation, photosynthetic bacteria may use the dark fermentation products, such as short chain organic acids and alcohols from the first stage, as a substrate to convert them into biohydrogen [67].

4.8. Potential future research directions

Nanotechnology applications have spread to the food, pharmaceutical, agricultural, and energy sectors [127]. Because of their distinct properties, including their nano size, structure, morphology, and reactivity, nanoparticles (NPs) have been identified as promising materials for enhanced biofuel processes. NPs are catalytic agents in the biofuel sector, serving as scavengers, electron transporters, inhibitors, and anaerobic consortium promoters. Their application in increased biohydrogen production results from their effects on intracellular electron transport, metalloenzyme activity, and microorganism growth. Because of its potential as a stimulant, iron is the metal most frequently used in photofermentation. More investigation is required to investigate additional possible metals or metal oxides for improved photo-fermentation hydrogen production. Most research has been done on a confined laboratory scale, so modifications to NPs' sizes, types, and shapes are necessary for scaling up photo-fermentation processes [59].

One way to overcome the primary limitation of photofermentation is to design an efficient photobioreactor that can distribute light uniformly and efficiently. Additionally, computational fluid dynamics simulation can be used to observe flow patterns before actual operations and comprehend constraints virtually, both of which aid in developing an effective photobioreactor [128].

The fermentation-based hydrogen production field can potentially revolutionize the energy industry, but current issues include low efficiency and high costs. Future perspectives should focus on optimizing the process with suitable substrates and understanding the microbiology involved in fermentative processes. This will help improve energy efficiency and ensure hydrogen production with diverse microbial communities. Understanding the microbiology involved in fermentative processes is crucial for achieving this goal [129].

The high cost of most photobioreactors is a barrier to industrial-scale photohydrogen production. The creation of advanced polymers that are impermeable to hydrogen could be a solution [130]. This upgrade can lower the reactors' costs and address a significant issue with the techniques' practical application.

Finally, anaerobic bacteria convert organic substrates into VFA and alcohols during dark fermentation, which produces biohydrogen. The generated metabolites could be targeted as substrates for purple non-sulfur bacteria to photo ferment, increasing the biohydrogen yield and decreasing the COD. Thus, designing a two-stage fermentation process through cultural condition optimization and using capable microorganisms may be a viable option for increased biohydrogen production and metabolite recovery. To increase the production of biohydrogen in large-scale processes by using dark and photofermentation, it is essential to use genetically engineered microorganisms that can use a wide range of substrates, require less nutrients, have enhanced stability, and are resistant to pretreatment inhibitors and contaminants. Additional methods for producing biohydrogen efficiently include using new technologies like immobilizing microorganisms, enhancing the cultural conditions that lead to their selection and enrichment, and modifying bioreactors to standardize process parameters [131,132].

5. Conclusion

With a high energy content and minimal to no environmental impact due to its utilization of organic waste biomass, biohydrogen is being explored as a viable option for a green, clean, and sustainable energy source. This paper reviewed recent research on biohydrogen production using various dark and photofermentation operational modes. The systematic content analysis and bibliometric review approach was used to review over two decades (i.e., 2000–2023) of research on the subject matter using research data from Scopus. The review disclosed a strong push to integrate hydrogen production into larger bioenergy systems, even though a lot of attention is still focused on improving the core process and removing obstacles. "Co-digestion" and "two-stage anaerobic digestion" are increasingly intricate, multi-step procedures that can potentially increase energy yields. The emphasis on "waste activated sludge" and "wastewater" draws attention to combining waste treatment with energy production to simultaneously address two pressing environmental issues. Co-digestion is a notable topic, indicating research into combining multiple feedstocks to improve process performance and economics. A hybrid system combining dark and photo fermentation, genetic engineering, biotechnological methods, and chemical application could enhance biohydrogen production yields. This system is more financially viable due to its lower cost per kilogram of hydrogen than standalone photo- and dark-fermentation processes. China leads the publishing world with 3455 publications, followed by the US with 808 and Italy with 738. India, Brazil, Spain, Japan, and South Korea publish between 400 and 600 articles, while Canada and the UK have around 400 publications each. Research is concentrated in East Asia, North America, and Europe, with China, the USA, and several European countries dominating the top positions.

CRediT authorship contribution statement

Ephraim Bonah Agyekum: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Flavio Odoi-Yorke:** Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Resources, Project administration, Methodology, Investigation, Formal analysis, Data curation.

Data availability

Data will be made available on request.

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Declaration of competing 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.

References

[1] Lanjekar PR, Panwar NL. A review on hydrogen production from biomass and commercialization assessment through technology readiness levels (TRLs). Bio Energy Res 2023;17:912–31. https://doi.org/10.1007/s12155-023-10697-1.
[2] Balachandar G, Varanasi JL, Singh V, Singh H, Das D. Biological hydrogen production via dark fermentation: a holistic approach from lab-scale to pilot-scale. Int J Hydrogen Energy 2020;45:5202–15. https://doi.org/10.1016/j.ijhydene.2019.09.006.
[3] Agyekum EB, Khan T, Odoi-Yorke F. Exploring the 3E, hydrogen, and ammonia creation potentials of a concentrated solar power (CSP) plant using an air-cooled condenser. Environ Sci Pollut Res 2024. https://doi.org/10.1007/s11356-024-34137-5.
[4] Jain R, Panwar NL, Chitranjan Agarwal, Gupta T. A comprehensive review on unleashing the power of hydrogen: revolutionizing energy systems for a sustainable future. Environ Sci Pollut Res 2024. https://doi.org/10.1007/s11356-024-33541-1.
[5] Qureshi F, Yusuf M, Kamyab H, Vo D-VN, Chelliapan S, Joo S-W, et al. Latest eco-friendly avenues on hydrogen production towards a circular bioeconomy: currents challenges, innovative insights, and future perspectives. Renew Sustain Energy Rev 2022;168:112916. https://doi.org/10.1016/j.rser.2022.112916.
[6] Nagarajan D, Lee D-J, Kondo A, Chang J-S. Recent insights into biohydrogen production by microalgae – from biophotolysis to dark fermentation. Bioresour Technol 2017;227:373–87. https://doi.org/10.1016/j.biortech.2016.12.104.
[7] Agyekum EB, Nutakor C, Khan T, Adegboye OR, Odoi-Yorke F, Okonkwo PC. Analyzing the research trends in the direction of hydrogen storage – a look into the past, present and future for the various technologies. Int J Hydrogen Energy 2024;74:259–75. https://doi.org/10.1016/j.ijhydene.2024.05.399.
[8] Chi J, Yu H. Water electrolysis based on renewable energy for hydrogen production. Chin J Catal 2018;39:390–4. https://doi.org/10.1016/S1872-2067(17)62949-8.
[9] Jin M, Wei X, Mu X, Ren W, Zhang S, Tang C, et al. Life-cycle analysis of biohydrogen production via dark-photo fermentation from wheat straw. Bioresour Technol 2024;396:130429. https://doi.org/10.1016/j.biortech.2024.130429.
[10] Lee B, Heo J, Kim S, Sung C, Moon C, Moon S, et al. Economic feasibility studies of high pressure PEM water electrolysis for distributed H2 refueling stations. Energy Convers Manag 2018;162:139–44. https://doi.org/10.1016/j.enconman.2018.02.041.
[11] Nadeem F, Zhang H, Tahir N, Zhang Z, Rani Singhania R, Shahzaib M, et al. Advances in the catalyzed photo-fermentative biohydrogen production through photo nanocatalysts with the potential of selectivity, and customization. Bioresour Technol 2023;382:129221. https://doi.org/10.1016/j.biortech.2023.129221.
[12] Guo XM, Trably E, Latrille E, Carrère H, Steyer J-P. Hydrogen production from agricultural waste by dark fermentation: a review. Int J Hydrogen Energy 2010;35:10660–73. https://doi.org/10.1016/j.ijhydene.2010.03.008.
[13] Karlsson A, Vallin L, Ejlertsson J. Effects of temperature, hydraulic retention time and hydrogen extraction rate on hydrogen production from the fermentation of food industry residues and manure. Int J Hydrogen Energy 2008;33:953–62. https://doi.org/10.1016/j.ijhydene.2007.10.055.
[14] Rai PK, Asthana RK, Singh SP. Optimization of photo-hydrogen production based on cheese whey spent medium. Int J Hydrogen Energy 2014;39:7597–603. https://doi.org/10.1016/j.ijhydene.2013.09.011.
[15] Ren N, Li J, Li B, Wang Y, Liu S. Biohydrogen production from molasses by anaerobic fermentation with a pilot-scale bioreactor system. Int J Hydrogen Energy 2006;31:2147–57. https://doi.org/10.1016/j.ijhydene.2006.02.011.
[16] Eroğlu E, Gündüz U, Yücel M, Türker L, Eroğlu İ. Photobiological hydrogen production by using olive mill wastewater as a sole substrate source. Int J

Hydrogen Energy 2004;29:163–71. https://doi.org/10.1016/S0360-3199(03)00110-1.

[17] Rai PK, Singh SP. Integrated dark- and photo-fermentation: recent advances and provisions for improvement. Int J Hydrogen Energy 2016;41:19957–71. https://doi.org/10.1016/j.ijhydene.2016.08.084.

[18] Ishaq H, Dincer I, Crawford C. A review on hydrogen production and utilization: challenges and opportunities. Int J Hydrogen Energy 2022;47:26238–64. https://doi.org/10.1016/j.ijhydene.2021.11.149.

[19] Luo M, Yi Y, Wang S, Wang Z, Du M, Pan J, et al. Review of hydrogen production using chemical-looping technology. Renew Sustain Energy Rev 2018;81:3186–214. https://doi.org/10.1016/j.rser.2017.07.007.

[20] Acar C, Dincer I. Review and evaluation of hydrogen production options for better environment. J Clean Prod 2019;218:835–49. https://doi.org/10.1016/j.jclepro.2019.02.046.

[21] Argun H, Kargi F. Bio-hydrogen production by different operational modes of dark and photo-fermentation: an overview. Int J Hydrogen Energy 2011;36:7443–59. https://doi.org/10.1016/j.ijhydene.2011.03.116.

[22] Arun J, Sasipraba T, Gopinath KP, Priyadharsini P, Nachiappan S, Nirmala N, et al. Influence of biomass and nanoadditives in dark fermentation for enriched bio-hydrogen production: a detailed mechanistic review on pathway and commercialization challenges. Fuel 2022;327:125112. https://doi.org/10.1016/j.fuel.2022.125112.

[23] Singh L, Wahid ZA. Methods for enhancing bio-hydrogen production from biological process: a review. J Ind Eng Chem 2015;21:70–80. https://doi.org/10.1016/j.jiec.2014.05.035.

[24] Ghimire A, Frunzo L, Pirozzi F, Trably E, Escudie R, Lens PNL, et al. A review on dark fermentative biohydrogen production from organic biomass: process parameters and use of by-products. Appl Energy 2015;144:73–95. https://doi.org/10.1016/j.apenergy.2015.01.045.

[25] Sillero L, Sganzerla WG, Forster-Carneiro T, Solera R, Perez M. A bibliometric analysis of the hydrogen production from dark fermentation. Int J Hydrogen Energy 2022;47:27397–420. https://doi.org/10.1016/j.ijhydene.2022.06.083.

[26] Nabgan W, Tuan Abdullah TA, Nabgan B, Jalil AA, Nordin AH, Ul-Hamid A, et al. Catalytic biohydrogen production from organic waste materials: a literature review and bibliometric analysis. Int J Hydrogen Energy 2021;46:30903–25. https://doi.org/10.1016/j.ijhydene.2021.04.100.

[27] Pan Y, Tao J, Yang S, Cui J, Xiong J, Lu X. Research trends and prospects for hydrogen production from sludge fermentation: based on bibliometric analysis. Waste Dispos Sustain Energy 2024. https://doi.org/10.1007/s42768-024-00190-6.

[28] Jannat FT, Aftab K, Kalsoom U, Baig MA. A bibliometric analysis of the role of nanotechnology in dark fermentative biohydrogen production. Environ Sci Pollut Res 2024;31:24815–35. https://doi.org/10.1007/s11356-024-33005-6.

[29] Al- Janabi SK, Barron AR, Shabbani HJK, Othman MR, Kim J. Advances in hydrogen production from sustainable resources through biological and thermochemical pathways: review and bibliometric analysis. Int J Hydrogen Energy 2024;60:28–45. https://doi.org/10.1016/j.ijhydene.2024.02.054.

[30] Agyekum EB, Ampah JD, Wilberforce T, Afrane S, Nutakor C. Research progress, trends, and current state of development on PEMFC-new insights from a bibliometric analysis and characteristics of two decades of research output. Membranes 2022;12:1103. https://doi.org/10.3390/membranes12111103.

[31] Kumar G, Shobana S, Nagarajan D, Lee D-J, Lee K-S, Lin C-Y, et al. Biomass based hydrogen production by dark fermentation — recent trends and opportunities for greener processes. Curr Opin Biotechnol 2018;50:136–45. https://doi.org/10.1016/j.copbio.2017.12.024.

[32] Mishra P, Krishnan S, Rana S, Singh L, Sakinah M, Ab Wahid Z. Outlook of fermentative hydrogen production techniques: an overview of dark, photo and integrated dark-photo fermentative approach to biomass. Energy Strategy Rev 2019;24:27–37. https://doi.org/10.1016/j.esr.2019.01.001.

[33] Levin DB, Pitt L, Love M. Biohydrogen production: prospects and limitations to practical application. Int J Hydrogen Energy 2004;29:173–85. https://doi.org/10.1016/S0360-3199(03)00094-6.

[34] Rai PK, Singh SP, Asthana RK. Biohydrogen production from cheese whey wastewater in a two-step anaerobic process. Appl Biochem Biotechnol 2012;167:1540–9. https://doi.org/10.1007/s12010-011-9488-4.

[35] Nath K, Kumar A, Das D. Hydrogen production by Rhodobacter sphaeroides strain O.U.001 using spent media of Enterobacter cloacae strain DM11. Appl Microbiol Biotechnol 2005;68:533–41. https://doi.org/10.1007/s00253-005-1887-4.

[36] Fan Q, Caserta G, Lorent C, Lenz O, Neubauer P, Gimpel M. Optimization of culture conditions for oxygen-tolerant regulatory [NiFe]-hydrogenase production from Ralstonia eutropha H16 in Escherichia coli. Microorganisms 2021;9:1195.

[37] Kou M, Wang Y, Xu Y, Ye L, Huang Y, Jia B, et al. Molecularly engineered covalent organic frameworks for hydrogen peroxide photosynthesis. Angew Chem Int Ed 2022;61:e202200413. https://doi.org/10.1002/anie.202200413.

[38] Teramoto H, Suda M, Inui M. Effects of potential inhibitors present in dilute acid-pretreated corn stover on fermentative hydrogen production by *Escherichia coli*. Int J Hydrogen Energy 2022;47:29219–29. https://doi.org/10.1016/j.ijhydene.2022.06.267.

[39] Wang H, Le Y, Sun J. Consolidated bioprocessing of biomass and synthetic cadmium wastewater substrates for enhancing hydrogen production by *Clostridium thermocellum*-CdS complex. Fuel 2022;316:123207. https://doi.org/10.1016/j.fuel.2022.123207.

[40] Zhang C, Li T, Su G, He J. Enhanced direct fermentation from food waste to butanol and hydrogen by an amylolytic *Clostridium*. Renew Energy 2020;153:522–9. https://doi.org/10.1016/j.renene.2020.01.151.

[41] Moura AGL, Rabelo CABS, Okino CH, Maintinguer SI, Silva EL, Varesche MBA. Enhancement of *Clostridium butyricum* hydrogen production by iron and nickel nanoparticles: effects on hydA expression. Int J Hydrogen Energy 2020;45:28447–61. https://doi.org/10.1016/j.ijhydene.2020.07.161.

[42] Lertsriwong S, Glinwong C. Newly-isolated hydrogen-producing bacteria and biohydrogen production by *Bacillus* coagulans MO11 and *Clostridium beijerinckii* CN on molasses and agricultural wastewater. Int J Hydrogen Energy 2020;45:26812–21. https://doi.org/10.1016/j.ijhydene.2020.07.032.

[43] Rosa D, Medeiros ABP, Martinez-Burgos WJ, do Nascimento JR, de Carvalho JC, Sydney EB, et al. Biological hydrogen production from palm oil mill effluent (POME) by anaerobic consortia and *Clostridium beijerinckii*. J Biotechnol 2020;323:17–23. https://doi.org/10.1016/j.jbiotec.2020.06.015.

[44] Son Y-S, Jeon J-M, Kim D-H, Yang Y-H, Jin Y-S, Cho B-K, et al. Improved bio-hydrogen production by overexpression of glucose-6-phosphate dehydrogenase and FeFe hydrogenase in *Clostridium acetobutylicum*. Int J Hydrogen Energy 2021;46:36687–95. https://doi.org/10.1016/j.ijhydene.2021.08.222.

[45] Chen L, Zhang K, Wang M, Zhang Z, Feng Y. Enhancement of magnetic field on fermentative hydrogen production by *Clostridium pasteurianum*. Bioresour Technol 2021;341:125764. https://doi.org/10.1016/j.biortech.2021.125764.

[46] Ramprakash B, Incharoensakdi A. Supplementation of magnetic nanoparticles for enhancement of dark fermentative hydrogen production from pretreated garden wastes using *Enterobacter aerogenes*. Fuel 2023;342:127857. https://doi.org/10.1016/j.fuel.2023.127857.

[47] Rao R, Basak N. Optimization and modelling of dark fermentative hydrogen production from cheese whey by *Enterobacter aerogenes* 2822. Int J Hydrogen Energy 2021;46:1777–800. https://doi.org/10.1016/j.ijhydene.2020.10.142.

[48] Boshagh F, Rostami K. Kinetic models of biological hydrogen production by Enterobacter aerogenes. Biotechnol Lett 2021;43:435–43. https://doi.org/10.1007/s10529-020-03051-4.

[49] Moreira FS, Rodrigues MS, Sousa LM, Batista FRX, Ferreira JS, Cardoso VL. Single-stage repeated batch cycles using co-culture of *Enterobacter cloacae* and purple non-sulfur bacteria for hydrogen production. Energy 2022;239:122465. https://doi.org/10.1016/j.energy.2021.122465.

[50] Ekwenna EB, Tabraiz S, Wang Y, Roskilly A. Exploring the feasibility of biological hydrogen production using seed sludge pretreated with agro-industrial wastes. Renew Energy 2023;215:118934. https://doi.org/10.1016/j.renene.2023.118934.

[51] Del Angel-Acosta YA, Alvarez LH, Garcia-Reyes RB, Garza-González MT, Carrillo-Reyes J. Addition of electron shuttling compounds and different pH conditions for hydrogen production by a heat-treated sludge. Biocatal Agric Biotechnol 2020;23:101507. https://doi.org/10.1016/j.bcab.2020.101507.

[52] Zhang Y, Ni J-Q, Liu C, Ke Y, Zheng Y, Zhen G, et al. Hydrogen production promotion and energy saving in anaerobic co-fermentation of heat-treated sludge and food waste. Environ Sci Pollut Res 2024. https://doi.org/10.1007/s11356-024-31851-y.

[53] Sliem MA, El-Ansary S, Soliman W, Badr Y. Enhancing biogas production of cow dung during anaerobic digestion using nanoferrites. Biomass Convers Biorefinery 2022;12:4139–46. https://doi.org/10.1007/s13399-021-01683-8.

[54] Nong HTT, Unpaprom Y, Whangchai K, Ramaraj R. Sustainable valorization of water primrose with cow dung for enhanced biogas production. Biomass Convers Biorefinery 2022;12:1647–55. https://doi.org/10.1007/s13399-020-01065-6.

[55] Deheri C, Mohanty AP, Acharya SK. An experimental approach to produce hydrogen from food waste, cow dung, and sludge solution. Mater Today Proc 2021;41:242–6. https://doi.org/10.1016/j.matpr.2020.08.801.

[56] Malolan R, Jayaraman RS, Adithya S, Arun J, Gopinath KP, SundarRajan P, et al. Anaerobic digestate water for *Chlorella pyrenoidosa* cultivation and employed as co-substrate with cow dung and chicken manure for methane and hydrogen production: a closed loop approach. Chemosphere 2021;266:128963. https://doi.org/10.1016/j.chemosphere.2020.128963.

[57] Deheri C, Acharya SK. Effect of calcium peroxide and sodium hydroxide on hydrogen and methane generation during the co-digestion of food waste and cow dung. J Clean Prod 2021;279:123901. https://doi.org/10.1016/j.jclepro.2020.123901.

[58] Budiman PM, Wu TY, Ramanan RN Md, Jahim J. Reusing colored industrial wastewaters in a photofermentation for enhancing biohydrogen production by using ultrasound stimulated Rhodobacter sphaeroides. Environ Sci Pollut Res 2017;24:15870–81. https://doi.org/10.1007/s11356-017-8807-x.

[59] Hitam CNC, Jalil AA. A review on biohydrogen production through photo-fermentation of lignocellulosic biomass. Biomass Convers Biorefinery 2023;13:8465–83. https://doi.org/10.1007/s13399-020-01140-y.

[60] Łukajtis R, Hołowacz I, Kucharska K, Glinka M, Rybarczyk P, Przyjazny A, et al. Hydrogen production from biomass using dark fermentation. Renew Sustain Energy Rev 2018;91:665–94. https://doi.org/10.1016/j.rser.2018.04.043.

[61] Melitos G, Voulkopoulos X, Zabaniotou A. Waste to sustainable biohydrogen production via photo-fermentation and biophotolysis − A systematic review. Renew Energy Environ Sustain 2021;6:45. https://doi.org/10.1051/rees/2021047.

[62] Akhlaghi N, Najafpour-Darzi G. A comprehensive review on biological hydrogen production. Int J Hydrogen Energy 2020;45:22492–512. https://doi.org/10.1016/j.ijhydene.2020.06.182.

[63] Ghosh S, Dairkee UK, Chowdhury R, Bhattacharya P. Hydrogen from food processing wastes via photofermentation using Purple Non-sulfur Bacteria (PNSB) – a review. Energy Convers Manag 2017;141:299–314. https://doi.org/10.1016/j.enconman.2016.09.001.

[64] Wu TY, Hay JXW, Kong LB, Juan JC, Jahim JMd. Recent advances in reuse of waste material as substrate to produce biohydrogen by purple non-sulfur (PNS)

bacteria. Renew Sustain Energy Rev 2012;16:3117–22. https://doi.org/10.1016/j.rser.2012.02.002.
[65] Guo S, Lu C, Wang K, Wang J, Zhang Z, Jing Y, et al. Enhancement of pH values stability and photo-fermentation biohydrogen production by phosphate buffer. Bioengineered 2020;11:291–300.
[66] Laocharoen S, Reungsang A. Isolation, characterization and optimization of photo-hydrogen production conditions by newly isolated *Rhodobacter sphaeroides* KKU-PS5. Int J Hydrogen Energy 2014;39:10870–82. https://doi.org/10.1016/j.ijhydene.2014.05.055.
[67] Luongo V, Ghimire A, Frunzo L, Fabbricino M, d'Antonio G, Pirozzi F, et al. Photofermentative production of hydrogen and poly-β-hydroxybutyrate from dark fermentation products. Bioresour Technol 2017;228:171–5. https://doi.org/10.1016/j.biortech.2016.12.079.
[68] Basak N, Das D. The prospect of purple non-sulfur (PNS) photosynthetic bacteria for hydrogen production: the present state of the art. World J Microbiol Biotechnol 2007;23:31–42. https://doi.org/10.1007/s11274-006-9190-9.
[69] Ananthi V, Bora A, Ramesh U, Yuvakkumar R, Raja K, Ponnuchamy K, et al. A review on the technologies for sustainable biohydrogen production. Process Saf Environ Protect 2024;186:944–56. https://doi.org/10.1016/j.psep.2024.04.034.
[70] Holladay JD, Hu J, King DL, Wang Y. An overview of hydrogen production technologies. Catal Today 2009;139:244–60. https://doi.org/10.1016/j.cattod.2008.08.039.
[71] Liu B-F, Ren N-Q, Tang J, Ding J, Liu W-Z, Xu J-F, et al. Bio-hydrogen production by mixed culture of photo- and dark-fermentation bacteria. Int J Hydrogen Energy 2010;35:2858–62. https://doi.org/10.1016/j.ijhydene.2009.05.005.
[72] Ding J, Liu B-F, Ren N-Q, Xing D-F, Guo W-Q, Xu J-F, et al. Hydrogen production from glucose by co-culture of *Clostridium Butyricum* and immobilized *Rhodopseudomonas faecalis* RLD-53. Int J Hydrogen Energy 2009;34:3647–52. https://doi.org/10.1016/j.ijhydene.2009.02.078.
[73] Liu B-F, Ren N-Q, Xing D-F, Ding J, Zheng G-X, Guo W-Q, et al. Hydrogen production by immobilized *R. faecalis* RLD-53 using soluble metabolites from ethanol fermentation bacteria *E. harbinense* B49. Bioresour Technol 2009;100: 2719–23. https://doi.org/10.1016/j.biortech.2008.12.020.
[74] Zhang Q, Zhang Z, Wang Y, Lee D-J, Li G, Zhou X, et al. Sequential dark and photo fermentation hydrogen production from hydrolyzed corn stover: a pilot test using 11 m3 reactor. Bioresour Technol 2018;253:382–6. https://doi.org/10.1016/j.biortech.2018.01.017.
[75] Meyer J, Kelley BC, Vignais PM. Effect of light nitrogenase function and synthesis in Rhodopseudomonas capsulata. J Bacteriol 1978;136:201–8. https://doi.org/10.1128/jb.136.1.201-208.1978.
[76] Agyekum EB. Evaluating the linkages between hydrogen production and nuclear power plants – a systematic review of two decades of research. Int J Hydrogen Energy 2024;65:606–25. https://doi.org/10.1016/j.ijhydene.2024.04.102.
[77] Ghosh A, Prasad VS. Off-grid Solar energy systems adoption or usage—a Bibliometric Study using the Bibliometrix R tool. Libr Philos Pract 2021;5673.
[78] Salmerón-Manzano E, Muñoz-Rodríguez D, Perea-Moreno A-J, Hernandez-Escobedo Q, Manzano-Agugliaro F. Worldwide scientific landscape on fires in photovoltaic. J Clean Prod 2024;461:142614. https://doi.org/10.1016/j.jclepro.2024.142614.
[79] Agyekum EB, Nutakor C. Recent advancement in biochar production and utilization – a combination of traditional and bibliometric review. Int J Hydrogen Energy 2023. https://doi.org/10.1016/j.ijhydene.2023.11.335.
[80] Agyekum EB, Odoi-Yorke F. Liquid air energy storage (LAES) – systematic review of two decades of research and future perspectives. J Energy Storage 2024;102: 114022. https://doi.org/10.1016/j.est.2024.114022.
[81] Agyekum EB, Odoi-Yorke F, Mbasso WF, Darko RO, Adegboye OR, Abbey AA. Towards a comprehensive understanding of atmospheric water harvesting technologies – a systematic and bibliometric review. Energy Rep 2024;12: 3795–811. https://doi.org/10.1016/j.egyr.2024.09.059.
[82] Thangavel P, Chandra B. Two decades of M-commerce consumer research: a bibliometric analysis using R biblioshiny. Sustainability 2023;15:11835.
[83] Huang J-H, Duan X-Y, He F-F, Wang G-J, Hu X-Y. A historical review and Bibliometric analysis of research on Weak measurement research over the past decades based on Biblioshiny. 2021.
[84] Reuters. China's SPIC plans $5. 9 billion investment turning green hydrogen into fuel. 2023.
[85] Global Times. China's green hydrogen investment tops 300 billion yuan in first nine months, leading the world. 2023.
[86] Nargotra P, Ortizo RGG, Wang J-X, Tsai M-L, Dong C-D, Sun P-P, et al. Enzymes in the bioconversion of food waste into valuable bioproducts: a circular economy perspective. Syst Microbiol Biomanufacturing 2024;4:850–68. https://doi.org/10.1007/s43393-024-00283-7.
[87] Kusumowardani N, Tjahjono B, Lazell J, Bek D, Theodorakopoulos N, Andrikopoulos P, et al. A circular capability framework to address food waste and losses in the agri-food supply chain: the antecedents, principles and outcomes of circular economy. J Bus Res 2022;142:17–31. https://doi.org/10.1016/j.jbusres.2021.12.020.
[88] Talukdar D. Patterns of research productivity in the business ethics literature: insights from analyses of bibliometric distributions. J Bus Ethics 2011;98:137–51. https://doi.org/10.1007/s10551-010-0539-5.
[89] Chen Q. Bibliometric analysis on the study of education informatization. In: Li S, Jin Q, Jiang X, Park JJ, editors. Front. Future dev. Inf. Technol. Med. Educ., vol. 269. Dordrecht: Springer Netherlands; 2014. p. 869–77. https://doi.org/10.1007/978-94-007-7618-0_85.
[90] Liu H, Grot S, Logan BE. Electrochemically assisted microbial production of hydrogen from acetate. Environ Sci Technol 2005;39:4317–20. https://doi.org/10.1021/es050244p.
[91] Hawkes F. Sustainable fermentative hydrogen production: challenges for process optimisation. Int J Hydrogen Energy 2002;27:1339–47. https://doi.org/10.1016/S0360-3199(02)00090-3.
[92] Hawkes F, Hussy I, Kyazze G, Dinsdale R, Hawkes D. Continuous dark fermentative hydrogen production by mesophilic microflora: principles and progress. Int J Hydrogen Energy 2007;32:172–84. https://doi.org/10.1016/j.ijhydene.2006.08.014.
[93] Guo XM, Trably E, Latrille E, Carrère H, Steyer J-P. Hydrogen production from agricultural waste by dark fermentation: a review. Int J Hydrogen Energy 2010; 35:10660–73. https://doi.org/10.1016/j.ijhydene.2010.03.008.
[94] Mizuno O, Dinsdale R, Hawkes FR, Hawkes DL, Noike T. Enhancement of hydrogen production from glucose by nitrogen gas sparging. Bioresour Technol 2000;73:59–65. https://doi.org/10.1016/S0960-8524(99)00130-3.
[95] Shin H. Hydrogen production from food waste in anaerobic mesophilic and thermophilic acidogenesis. Int J Hydrogen Energy 2004;29:1355–63. https://doi.org/10.1016/j.ijhydene.2003.09.011.
[96] Kim S. Feasibility of biohydrogen production by anaerobic co-digestion of food waste and sewage sludge. Int J Hydrogen Energy 2004;29:1607–16. https://doi.org/10.1016/j.ijhydene.2004.02.018.
[97] Antonopoulou G, Gavala HN, Skiadas IV, Angelopoulos K, Lyberatos G. Biofuels generation from sweet sorghum: fermentative hydrogen production and anaerobic digestion of the remaining biomass. Bioresour Technol 2008;99:110–9. https://doi.org/10.1016/j.biortech.2006.11.048.
[98] Ren N, Li J, Li B, Wang Y, Liu S. Biohydrogen production from molasses by anaerobic fermentation with a pilot-scale bioreactor system. Int J Hydrogen Energy 2006;31:2147–57. https://doi.org/10.1016/j.ijhydene.2006.02.011.
[99] Chen W, Tseng Z, Lee K, Chang J. Fermentative hydrogen production with CGS5 isolated from anaerobic sewage sludge. Int J Hydrogen Energy 2005;30:1063–70. https://doi.org/10.1016/j.ijhydene.2004.09.008.
[100] Lin C. Carbon/nitrogen-ratio effect on fermentative hydrogen production by mixed microflora. Int J Hydrogen Energy 2004;29:41–5. https://doi.org/10.1016/S0360-3199(03)00083-1.
[101] Chang F. Biohydrogen production using an up-flow anaerobic sludge blanket reactor. Int J Hydrogen Energy 2004;29:33–9. https://doi.org/10.1016/S0360-3199(03)00082-X.
[102] Luo G, Angelidaki I. Integrated biogas upgrading and hydrogen utilization in an anaerobic reactor containing enriched hydrogenotrophic methanogenic culture. Biotechnol Bioeng 2012;109:2729–36. https://doi.org/10.1002/bit.24557.
[103] Hori T, Haruta S, Ueno Y, Ishii M, Igarashi Y. Dynamic transition of a methanogenic population in response to the concentration of volatile fatty acids in a thermophilic anaerobic digester. Appl Environ Microbiol 2006;72:1623–30. https://doi.org/10.1128/AEM.72.2.1623-1630.2006.
[104] Venkata Mohan S, Lalit Babu V, Sarma PN. Anaerobic biohydrogen production from dairy wastewater treatment in sequencing batch reactor (AnSBR): effect of organic loading rate. Enzym Microb Technol 2007;41:506–15. https://doi.org/10.1016/j.enzmictec.2007.04.007.
[105] Wang CC, Chang CW, Chu CP, Lee DJ, Chang B-V, Liao CS. Producing hydrogen from wastewater sludge by *Clostridium bifermentans*. J Biotechnol 2003;102: 83–92. https://doi.org/10.1016/S0168-1656(03)00007-5.
[106] Valdez-Vazquez I, Ríos-Leal E, Esparza-García F, Cecchi F, Poggi-Varaldo HM. Semi-continuous solid substrate anaerobic reactors for H2 production from organic waste: mesophilic versus thermophilic regime. Int J Hydrogen Energy 2005;30:1383–91. https://doi.org/10.1016/j.ijhydene.2004.09.016.
[107] Venetsaneas N, Antonopoulou G, Stamatelatou K, Kornaros M, Lyberatos G. Using cheese whey for hydrogen and methane generation in a two-stage continuous process with alternative pH controlling approaches. Bioresour Technol 2009;100: 3713–7. https://doi.org/10.1016/j.biortech.2009.01.025.
[108] Chen C-Y, Yang M-H, Yeh K-L, Liu C-H, Chang J-S. Biohydrogen production using sequential two-stage dark and photo fermentation processes. Int J Hydrogen Energy 2008;33:4755–62. https://doi.org/10.1016/j.ijhydene.2008.06.055.
[109] Yang P, Zhang R, McGarvey JA, Benemann JR. Biohydrogen production from cheese processing wastewater by anaerobic fermentation using mixed microbial communities. Int J Hydrogen Energy 2007;32:4761–71. https://doi.org/10.1016/j.ijhydene.2007.07.038.
[110] Lin C-Y, Lay CH. Effects of carbonate and phosphate concentrations on hydrogen production using anaerobic sewage sludge microflora. Int J Hydrogen Energy 2004;29:275–81. https://doi.org/10.1016/j.ijhydene.2003.07.002.
[111] Luo G, Xie L, Zhou Q, Angelidaki I. Enhancement of bioenergy production from organic wastes by two-stage anaerobic hydrogen and methane production process. Bioresour Technol 2011;102:8700–6. https://doi.org/10.1016/j.biortech.2011.02.012.
[112] Safari F, Dincer I. Development and analysis of a novel biomass-based integrated system for multigeneration with hydrogen production. Int J Hydrogen Energy 2019;44:3511–26. https://doi.org/10.1016/j.ijhydene.2018.12.101.
[113] Zhu H, Stadnyk A, Béland M, Seto P. Co-production of hydrogen and methane from potato waste using a two-stage anaerobic digestion process. Bioresour Technol 2008;99:5078–84. https://doi.org/10.1016/j.biortech.2007.08.083.
[114] Steinbusch KJJ, Hamelers HVM, Plugge CM, Buisman CJN. Biological formation of caproate and caprylate from acetate: fuel and chemical production from low grade biomass. Energy Environ Sci 2011;4:216–24. https://doi.org/10.1039/C0EE00282H.
[115] Zhao Z, Li Y, Quan X, Zhang Y. Towards engineering application: potential mechanism for enhancing anaerobic digestion of complex organic waste with

different types of conductive materials. Water Res 2017;115:266–77. https://doi.org/10.1016/j.watres.2017.02.067.

[116] Yang Y, Zhang Y, Li Z, Zhao Z, Quan X, Zhao Z. Adding granular activated carbon into anaerobic sludge digestion to promote methane production and sludge decomposition. J Clean Prod 2017;149:1101–8. https://doi.org/10.1016/j.jclepro.2017.02.156.

[117] Chen W, Chen S, Kumarkhanal S, Sung S. Kinetic study of biological hydrogen production by anaerobic fermentation. Int J Hydrogen Energy 2006;31:2170–8. https://doi.org/10.1016/j.ijhydene.2006.02.020.

[118] Mus F, Dubini A, Seibert M, Posewitz MC, Grossman AR. Anaerobic acclimation in chlamydomonas reinhardtii. J Biol Chem 2007;282:25475–86. https://doi.org/10.1074/jbc.M701415200.

[119] Lim S-J, Kim BJ, Jeong C-M, Choi J, Ahn YH, Chang HN. Anaerobic organic acid production of food waste in once-a-day feeding and drawing-off bioreactor. Bioresour Technol 2008;99:7866–74. https://doi.org/10.1016/j.biortech.2007.06.028.

[120] Lee H-S, Vermaas WF, Rittmann BE. Biological hydrogen production: prospects and challenges. Trends Biotechnol 2010;28:262–71.

[121] Hay JXW, Wu TY, Juan JC, Md Jahim J. Biohydrogen production through photo fermentation or dark fermentation using waste as a substrate: overview, economics, and future prospects of hydrogen usage. Biofuels Bioprod Biorefining 2013;7:334–52. https://doi.org/10.1002/bbb.1403.

[122] Lin C-Y, Lay C-H, Sen B, Chu C-Y, Kumar G, Chen C-C, et al. Fermentative hydrogen production from wastewaters: a review and prognosis. Int J Hydrogen Energy 2012;37:15632–42. https://doi.org/10.1016/j.ijhydene.2012.02.072.

[123] Zhu H, Parker W, Basnar R, Proracki A, Falletta P, Béland M, et al. Biohydrogen production by anaerobic co-digestion of municipal food waste and sewage sludges. Int J Hydrogen Energy 2008;33:3651–9. https://doi.org/10.1016/j.ijhydene.2008.04.040.

[124] Tiang MF, Fitri Hanipa MA, Abdul PM, Jahim JMd, Mahmod SS, Takriff MS, et al. Recent advanced biotechnological strategies to enhance photo-fermentative biohydrogen production by purple non-sulphur bacteria: an overview. Int J Hydrogen Energy 2020;45:13211–30. https://doi.org/10.1016/j.ijhydene.2020.03.033.

[125] Saratale GD, Chen S-D, Lo Y-C, Saratale RG, Chang J-S. Outlook of biohydrogen production from lignocellulosic feedstock using dark fermentation. Review. J Sci Ind Res 2008;67(11):962–79.

[126] Das D, Veziroglu TN. Advances in biological hydrogen production processes. Int J Hydrogen Energy 2008;33:6046–57. https://doi.org/10.1016/j.ijhydene.2008.07.098.

[127] Nadeem F, Jiang D, Tahir N, Alam M, Zhang Z, Yi W, et al. Defect engineering in SnO2 nanomaterials: pathway to enhance the biohydrogen production from agricultural residue of corn stover. Appl Mater Today 2020;21:100850. https://doi.org/10.1016/j.apmt.2020.100850.

[128] Das SR, Basak N. Molecular biohydrogen production by dark and photo fermentation from wastes containing starch: recent advancement and future perspective. Bioproc Biosyst Eng 2021;44:1–25. https://doi.org/10.1007/s00449-020-02422-5.

[129] Dari DN, Freitas IS, Aires FI da S, Melo RLF, dos Santos KM, da Silva Sousa P, et al. An updated review of recent applications and perspectives of hydrogen production from biomass by fermentation: a comprehensive analysis. Biomass 2024;4:132–63.

[130] Hallenbeck PC, Abo-Hashesh M, Ghosh D. Strategies for improving biological hydrogen production. Bioresour Technol 2012;110:1–9. https://doi.org/10.1016/j.biortech.2012.01.103.

[131] Sarangi PK, Nanda S. Biohydrogen production through dark fermentation. Chem Eng Technol 2020;43:601–12. https://doi.org/10.1002/ceat.201900452.

[132] Kumar G, Zhen G, Sivagurunathan P, Bakonyi P, Nemestóthy N, Bélafi-Bakó K, et al. Biogenic H2 production from mixed microalgae biomass: impact of pH control and methanogenic inhibitor (BESA) addition. Biofuel Res J 2016;3:470–4.