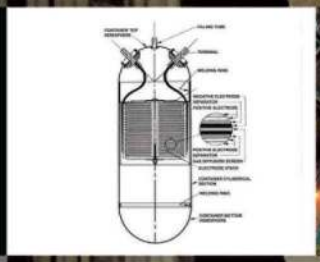
MATERIALS FOR HYDROGEN PRODUCTION, CONVERSION, AND STORAGE



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Contents

Preface

The extensive awareness and environmental concern are driving the global civilization towards cleaner and green energy production. This ultimately leaves no option other than using hydrogen as a fuel that has almost no adverse environmental impact. But hydrogen poses several hazards in terms of human safety as its mixture of air is prone to potential detonations and invisible fires. The permeability of cryogenic storage can induce frostbite as it leaks through metal pipes. In short, there are a lot of challenges at every step to strive for emission-free fuel. As the density of hydrogen is very low, efficient methods are being developed and engineered to store it in a small volume. Hydrogen can leak at a rate as low as 4 μg/sec to catch fire hazards and thus its detection poses a serious challenge both in terms of safety and expense. Both renewal and non-renewal sources are targeted as feedstocks for the production of hydrogen. The non-renewal feedstocks mainly of petroleum are the major contributor to date but there is a future perspective in renewal source comprising mainly of water splitting *via* electrolysis, radiolysis, thermolysis, photocatalytic water splitting, and biohydrogen routes which are being extensively worked out. When American physicist Richard Feynman said, "There is plenty of room at the bottom", material science filled plenty of scope for improved properties that can be exploited to overcome the enormous challenge of harnessing energy from hydrogen.This book edition mainly targets the current and future material for the production, conversion, and storage of the cleaner fuel – hydrogen. The scope and limitations both in terms of engineering and cost have been discussed.

Materials for Hydrogen Production, Conversion, and Storage describes mainly the production of hydrogen from various sources along with the protagonist materials involved. Further, the extensive and novel material involved in conversion technologies is discussed. The book also covered the details of storage materials of hydrogen for both physical and chemical systems. This book should be useful for engineers, environmentalists,

governmental policy planners, non-governmental organizations, faculty, researchers, students from academics, and laboratories that are linked to various functional materials related to hydrogen production, conversion, and storage capacity. Based on the book's objective, this issue edition is divided into 22 chapters:

Chapter 1 summarizes the possibility of hydrogen production from water in the solar-driven processes in the presence of transition metal oxides. Photo(electro)catalytic and thermochemical paths are described, with detailed characteristics, challenges, and problems. Lastly, future possibilities of the most popular metal oxide-based semiconductors are covered.
Chapter 2 discusses the role of lignin as a renewable and sustainable energy source and its valorization through feasible methods. This chapter mainly focuses on the catalytic conversion of lignin into value-added fuels which has the potential to meet the energy gap between the demand and supply of conventional fossil fuels.
Chapter 3 details various solar-hydrogen coupling hybrid systems for green energy applications. Photo-, electro-, thermo-, and bio-chemical solar systems to hydrogen production are also discussed. The classification of these systems, their fundamentals, and their components is presented as well, in addition to the future perspective for green energy applications.
Chapter 4 includes various methods of conversion of solar energy into hydrogen. This includes concentrated solar thermal H_2 production; thermo-chemical aqua splitting technology for solar-H_2 production; solar-H_2 through de-carbonization of fossil fuels; solar cracking; and solar thermal-based hydrogen generation through electrolysis and photovoltaic based hydrogen production.
Chapter 5 encompasses the role of electrocatalysts in electrocatalytic water splitting hydrogen evolution reaction. The basic mechanism of hydrogen evolution reaction and the significant parameters that qualify an efficient electrocatalyst are discussed. Various state-of-art catalysts for electrocatalytic generation of hydrogen through water splitting are also discussed.
Chapter 6 mainly focuses on the modern advancements in the composition and formulating of nanostructured catalysts of noble/non-noble metal-based materials for hydrogen evolution reactions (HER). The key challenges, perspectives, and opportunities for developing new catalysts for efficient electrochemical water splitting are also discussed.
Chapter 7 presents the biohydrogen production associated with the generation of secondary metabolites through dark fermentation. Details of principal metabolic pathways from specific organic wastes and principal microbiota involved are discussed. Additionally, it shows bioreactor

projects' main advances in biomass and operational optimization in wastewater-fed bioH_2-producing systems.

Chapter 8 describes the process of electrocatalytic water splitting for hydrogen production. The electrocatalyst foundations for water splitting, as well as the characteristics of a good electrocatalyst for hydrogen, are also discussed.

Chapter 9 highlights the prevailing issues associated with bioreactor operation and the recent advancement in alleviating the challenges of biohydrogen production. Four challenges are identified and discussed, namely physical, biological, chemical, and economical.

Chapter 10 addresses various microbes used in continuous hydrogen production from a large array of wastewaters. Photo-fermentation, dark fermentation, and microbial electrolytic cells are discussed in detail. Continuous hydrogen production is emphasized. Factors that affect hydrogen yield and hydrogen production rate are also discussed.

Chapter 11 reviews several conversion techniques for hydrogen evolution by water splitting using photocatalysis, photoelectrocatalysis, and photovoltaic-photoelectrochemical systems. On top of that, several types of membrane separation for hydrogen recovery are also discussed.

Chapter 12 emphasizes the applications of geothermal energy for hydrogen production that can be used as the principal energy carrier in the upcoming hydrogen era. The methods of hydrogen synthesis, thermodynamic efficiencies, economy, and environmental impacts are elaborated. Hence, this chapter brushes a portrait of a hydrogen-based greener sustainable future.

Chapter 13 provides the current advancements in design and morphology changes of g-C_3N_4 including porous, crystalline, thin-nanosheets, metal-doping/g-C_3N_4, and semiconductor/g-C_3N_4 heterogeneous photocatalysts for improving the H_2 production by photocatalytic water splitting. Moreover, the fundamental challenges and future outlooks herein photocatalytic water splitting for the evolution of H_2 energy are highlighted.

Chapter 14 elaborates the sustainable production of hydrogen by using graphitic carbon nitride (g-C_3N_4), as the utilization of g-CN in H_2 with high specific surface area transformations, power modules, sun-oriented cells, supercapacitors, and lithium batteries offers new freedoms. This record gives an examination of the effect of ecological testing on hydrogen-producing innovation from sustainable and non-renewable sources, with an accentuation on its utilization.

Chapter 15 recapitulates the fundamentals behind anaerobic digestion to produce hydrogen and highlighted the challenges and mitigation strategies

in biohydrogen production. Finally, the practicality of anaerobic digestion technologies at an industrial scale is discussed.

Chapter 16 presents information about the synthesis of hydrogen as an alternative to fossil fuel from abundantly available waste-activated sludge. Dark fermentation, photo fermentation, and microbial electrolysis cell methods used for hydrogen production are also discussed. Moreover, this chapter also explains various physical, chemical, and physicochemical treatments adopted to produce hydrogen along with the process conditions maintained.

Chapter 17 briefly describes the disadvantages of using fossil fuels. Recently, BioH_2 is considered as an alternative for fossil fuels as it can be generated from renewable sources like biomass and wastes. This chapter concentrates on the prospective use of waste-activated sludge as raw material for H_2 generation.

Chapter 18 enumerates the basic principle of perovskite materials, including the structure of oxide and halide perovskites with the synthesis processes. Various modifications of the perovskite materials are discussed. The recent developments in solar water splitting for hydrogen production, including photocatalysis, photoelectrochemical, and photovoltaic-electrocatalysis are reviewed in this chapter.

Chapter 19 briefly discusses the mechanism involved in hydrogen production with the help of a photocatalyst. Additionally, the role of co-catalyst and sacrificial reagent are discussed. Also, previously reported different nickel/nickel-based photocatalysts for hydrogen production are discussed in detail.

Chapter 20 explains the concept of waste-activated sludge used for the production of hydrogen-based on thermochemical and biological processes. The potential strategies and prospects of thermochemical and biological processes for hydrogen energy systems are well compared and presented based on their advantages, drawbacks, and future feasibility.

Chapter 21 showcases hydrogen storage potential and the general mechanism involved in hydrogen storage by metal-organic frameworks (MOFs). Furthermore, the effect of structural modifications of MOFs to enhance their H_2 storage capacities is discussed. Future recommendations are also outlined to overcome existing drawbacks in MOFs structure to make them acceptable for commercial H_2 storage.

Chapter 22 presents an overview of the most prominent high-density solids that are potential hydrogen storage materials and are anticipated as key enablers for the hydrogen economy. The aspects of hydrogen storage capacity, kinetics, and thermodynamics are briefly discussed for each class of materials in addition to their limitations and performance enhancement techniques.

Highlights:

- Provides a broad overview of present and upcoming materials for the hydrogen generation, conversion, and storage
- Introduces the readers and professionals with a solid foundation in the broad and expanding field of hydrogen generation, conversion, and storage
- Explores current procedures used in the production of hydrogen
- Details of hydrogen as an alternate source of energy from fossil fuels, water resources, and biomass

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9

Challenges and Mitigation Strategies Related to Biohydrogen Production

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Abstract

Although many studies related to biohydrogen have been reported, the productivity of biohydrogen production remains low. To achieve its implementation at an industrial scale, higher productivity is critical. Research on various bioreactor configurations and factors influencing hydrogen production has also been extensively investigated for mass production. Therefore, a review of the prevailing issues associated with bioreactor operation and the recent advancement in alleviating the challenges of biohydrogen production will be discussed in this chapter. Four challenges have been identified, namely, physical, biological, chemical, and economical, which enhancement strategies for improving biohydrogen productivity accompany each challenge.

***Keywords*:** Biohydrogen, bioreactor, biomass washout, bioaugmentation, inhibitors, techno-economic analysis

9.1 Introduction

The global energy demand is primarily met by non-renewable fossil-based fuels, which produce a range of toxic gases during combustion, such as carbon dioxide, carbon monoxide, and sulphur dioxide. The production and

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emission of these harmful gases pollute the environment. This situation leads to progressive research efforts seeking an alternative fuel that should be produced by renewable sources, which is eco-friendly. In this regard, anaerobic digestion fulfills the requirement which adopting the waste-to-wealth concept.

Anaerobic digestion involves a sequential biochemical reaction conducted by five groups of different microorganisms. The digestion process commenced with the microbial decomposition of organic matter into smaller derivative molecules with concurrent biohydrogen production and acid, which eventually transformed into methane and CO_2. Moreover, bioreactor configuration and design factors are vital parameters influencing the microbial growth environment [1]. A favorable microbial growth could increase the biohydrogen production efficiency for a long-term operation and could withstand a shock load. Biohydrogen production is frequently carried out in a continuous stirred tank reactor (CSTR). Many studies have intensified the focus on reactor optimization and operational control for a different type of substrate containing glucose [2, 3], sucrose [4], starch [2, 5], and cellulose [6].

It should be noted that the biomass contained in the CSTR is in suspended form. At low hydraulic retention time (HRT), the biomass is susceptible to being washed out and tends to mix with liquor concentrate, causing a reduction in biohydrogen production. It has been suggested that self-granulated biomass can be employed, resulting in doubled biomass retention time more significant than the HRT effect, supporting the slowly growing microorganisms favoring biohydrogen production [7]. Biohydrogen production can also be increased with the addition of different inoculums. Murugan *et al.* achieved a maximum hydrogen production of 566.44 mL/L by inserting *Acinetobacter junii*-AH4 inoculum into industrial wastewater [8]. An alternative to granular form, biomass can also be immobilized in biofilms consist of pristine and mixed cultures [9, 10]. This method has improved substrate degradation, biomass retention time, and biohydrogen production [11–13]. Load shock and heat shock treatment in the early operation also has been suggested could suppress methanogen growth, thus enhances biohydrogen production [14]. Notably, adjustment to operational control promotes the enhancement of biohydrogen production through anaerobic fermentation.

The challenge of utilizing biohydrogen in real application relies on its competitiveness with the existing fuel sources regarding fuel price and efficiency. The determination of fuel price is based on the working capital and capital fixed cost, which will be elaborated further in the next

subchapter. Research on biohydrogen production has now been geared towards improving production efficiency through process optimization and the exploitation of byproducts into a valuable compound supporting the circular biohydrogen economy [15, 16].

In this chapter, four prevailing limitations of biohydrogen production from anaerobic digestion typically processed in bioreactors have been categorized into physical, biological, chemical, and economic (Figure 9.1). The reported enhancement strategies for each limitation will be discussed accordingly.

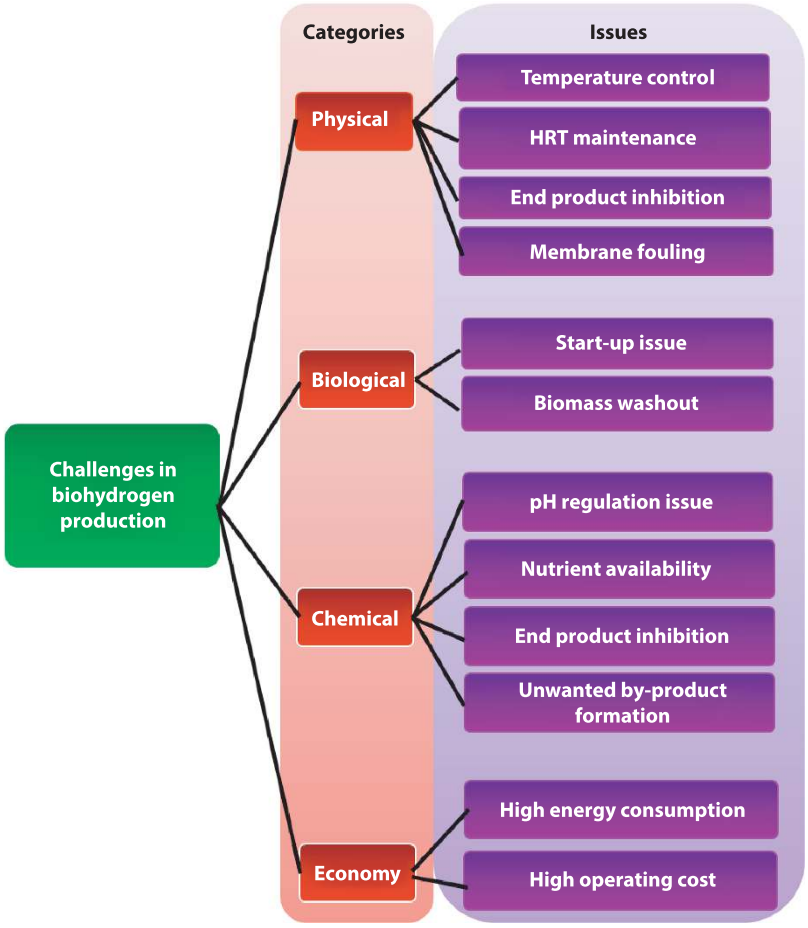

Figure 9.1 Prevailing challenges in biohydrogen production.

9.2 Limitation and Mitigation Approaches of Biohydrogen Production

Biohydrogen production refers to the biological activities in a bioreactor system to produce hydrogen from organic substrates. Hydrogen is an exciting energy carrier and is expected to play an essential role in the future due to zero pollution and high energy content [17]. However, biohydrogen production technologies are still in their infancy. Various limitations and constraints in the bioreactor, such as design and configuration, operation parameters, performance stability, substrate utilization and microbe used, and cost operation, are still not entirely resolved [18]. From this point forward, only prevailing challenges and their mitigation strategies related to biohydrogen production in a bioreactor, involving physical, biological, chemical, and economic, will be discussed.

9.2.1 Physical Issues and Their Mitigation Approaches

9.2.1.1 Operating Temperature Issue and Its Control

Studies showed that temperature must be controlled during biohydrogen production, because the temperature variation affects productivity. Biohydrogen production at an industrial scale is performed at mesophilic conditions (20–45°C). Working in mesophilic conditions offers simplicity on bioreactor handling and low cost due to low energy consumption. However, the biohydrogen yield at mesophilic conditions is comparably lesser than that at thermophilic conditions. For instance, biohydrogen production at thermophilic conditions achieved 1.03 mol H_2/mol [20], while 0.78 mol H_2/mol at mesophilic conditions [19]. Increasing temperature to thermophilic conditions tends to improve biohydrogen yield. However, rising in temperature may also reduce biohydrogen production. Lee *et al.* [21] reported that the higher temperature might cause denaturation on the enzyme; consequently, the biomass growth or granule formation is inhibited. Additionally, the main drawback of thermophilic conditions for biohydrogen production is high-cost operation and high energy consumption. In terms of cost, the mesophilic process is preferable than the thermophilic when the bioreactors are applied at an industrial scale.

9.2.1.2 Hydraulic Retention Time (HRT) and Optimization

Hydraulic retention time (HRT) can be defined as the total time required by a unit of a substrate to be approached by the microorganism in a bioreactor

to produce the bioconversion of interest [21]. HRT is generally associated with the reaction rate (related to the concentration and type of substrate), appropriate cells (single- or mixed cells), and operating temperature. In the dark fermentation system, the optimum HRT for biohydrogen production is obtained around a few hours to one day [23–25], while biomethane production lasts for a few days [22]. Biohydrogen production is incompatible at the longer HRT because the metabolic route changes from acidogenic to methanogenic. The longer HRT of 72 hours leads to reduce biohydrogen generation. Also, other research showed that the biohydrogen production from olive mill effluent was low at the longer HRT [23]. This observation might be due to the washout phenomena on active biomass in the bioreactor [21]. In general, biomethane production is reduced with reducing HRT (i.e., 2–10 h) attributed to the poor growth of methanogenic [24]. A study reported that by reducing the HRT to seven-fold (7 days to 1 day) resulted in the 30-fold increment of biohydrogen [23]. Therefore, one of the strategies to solve low biohydrogen production is by reducing the HRT.

9.2.1.3 High Hydrogen Partial Pressure – Implication and Overcoming the Issue

Inhibition and reduction of biohydrogen generation are caused by the accumulation of hydrogen in a liquid phase (refers to the high partial pressure) [25–27]. Thermodynamically, proton reduction to hydrogen is unfavorable at the high hydrogen concentration in a liquid phase. As a result, oxidation of hydrogen to proton is preferable and simultaneously reduces hydrogen production. In addition, biohydrogen production could also be reduced under high hydrogen partial pressure due to the conversion of long-chain fatty acids to hydrogen and acetate [28]. Moreover, the rise in hydrogen partial pressure may lead to metabolic route shift to lactic acid, acetic, acetone, and/or butanol with the reduction of hydrogen yield [29, 30]. Lowering hydrogen partial pressure to 20% with an interval of 2 hours led to improved biohydrogen production efficiency and yield of 54% and 202.15 mL, respectively, compared to the control [31].

Approaches such as increased headspace volume [27], continuous-release gas [32], and inert gas (i.e., N_2 or CO_2) sparging or stripping vacuum can be employed [33]. In general, the approaches used are based on the type of reactor and its application. The stirring of substrate and culture is the most straightforward approach to reduce the hydrogen partial pressure. Also, the hydrogen partial pressure can be reduced by eliminating the hydrogen pressure in the liquid phase and gas through the N_2 sparging.

An automated control of hydrogen partial pressure can also be executed by installing a hydrogen sensor inside the bioreactor to bring down the pressure equal to ambient pressure, as demonstrated by Das *et al.* [34].

9.2.1.4 Membrane Fouling Issues and Solutions

Another crucial issue in the anaerobic bioreactor is membrane fouling. The accumulation of foulants causes the membrane fouling to form a crust on the membrane surface; consequently, blocking pore, reducing membrane permeability, and declining flux density [35–37]. This issue may increase the operational cost as a whole. Generally, membrane fouling is affected by three aspects; operational parameters, physicochemical, and biological (Table 9.1).

Type of fouling can be classified into biological fouling (biofouling), organic and inorganic fouling [53]. Biofouling referred to the fouling condition caused by the growth of microbe cells and deposited on the surface

Table 9.1 Some typical parameters influencing membrane fouling.

Parameters	**Properties**	**Ref.**
Operational	Hydraulic retention time (HRT)	[21, 38, 39]
	Temperature	[40]
	pH	[41]
	Organic loading rate (OLR)	[42, 43]
	Shear rate	[44]
Physicochemical	Backwash	[45]
	Flocculant/Coagulant	[46]
	Chemical cleaning	[47, 48]
	Physical scouring	[47, 48]
	Salinity	[49]
Biological	Biomass	[38, 50, 51]
	Bacteriophages	[48, 51]
	Cell wall hydrolysis	[48]
	Type of activated sludge	[49, 52]

or pore membrane. Microbial growth tends to form biofilm on the membrane surface, which contribute the bioreactor performance. In a bioelectrochemical system, a high microbe density on the membrane surface tends to block the protons transportation from anode to cathode, leading to membrane fouling and reducing bioreactor performance [54]. On the other hand, organic fouling is caused by the deposition of substances, for instance, protein, polysaccharides, humic, and various organic [45]. Meanwhile, inorganic fouling is caused by the accumulation of chemical elements, e.g., magnesium, calcium silica aluminium, silica, and inorganic and organic biological compound on the membrane [46]. Chemical precipitation formed via the interaction of anions and metal cations could slit through the membrane pores, eventually contributed to the inorganic fouling.

Numerous techniques such as modification of bioreactor operation system involving period of the filtration cycle, backwashing, flow rate tuning have been used to minimize the fouling on the membrane. Moreover, chemical cleaning, intensified aeration (for aerobic reactor), ultrasonic irradiation, membrane pre-treatment and membrane surface modification are also considered as alternative techniques to mitigate membrane fouling [55]. The conventional approaches (i.e., membrane backwashing and relaxation) can also be adopted to minimize fouling on the membrane and improve the bioreactor performance. Of the traditional techniques, the sonification could break down biofilm into micro fragments, which then entering membrane pores; thereby, the sonification is only practical for complex fouling conditions [56]. Membrane fouling can also be treated using chemical cleaners such as hydrochloric acid, ethylene diamine tetraacetate (EDTA), citric acid, nitric acid, hypochlorite, and NaOH. Bear in mind that the chemical technique to treat the membrane may cause damage in membrane performance and reduce its lifespan [53].

Activated carbon and zeolite can eliminate colloids and soluble compounds to reduce fouling on the membrane [57]. Antifouling agents such as polymerizable bi-continuous microemulsion (PBM) can be used to prevent fouling in ultrafiltration membranes. In addition, nanoparticles, for instance, titanium oxide (TiO) and zinc oxide (ZnO), carbon nanotubes (CNTs), nanosilver, graphene, and fullerene can also be utilized as antifouling agents given their high stability against microbial activities [58]. Among these nanoparticles, CNTs shows the best performance to prevent fouling membrane [59, 60].

9.2.2 Biological Issues and Their Mitigation Approaches

9.2.2.1 Start-Up Issue and Improvement Through Bioaugmentation

A continuous biohydrogen production can be guaranteed by overcoming the start-up issue of microbial culture in the bioreactor. Start-up remains a significant issue associated with the time needed to achieve stable performance. A review study has identified parameters responsible for alleviating the start-up issue, including bioreactors' design, the acclimation of hydrogen-producing microbes population, and shift over fermentation mode [61]. Formulating fermentation media, including food to microbe ratio control, pre-determined culture supplement, and the reducing agent has also been proven to overcome the start-up issue, consequently improving bioreactor performance and increasing the biohydrogen yield [62]. Substrate concentration, composition, and the microbes' metabolic properties also influence the whole biohydrogen production when harvested from a mixed culture.

One of the practical strategies to achieve an improved start-up culture and high substrate conversion efficiency is through bioaugmentation strategies by inoculating preferred microbial strains to the existing microbial population in the fermentation media [63]. Through bioaugmentation effort, the inoculation of single or mixed native microflora with *C. acetobutylicum* [64], acidogenic consortia [65], and hydrogen-producing microbes [66] has been demonstrated to enhance production efficiency. In the same effort, bioaugmentation has also been proven effective to improve bioreactor performance [67], regaining the start-up of a bioreactor [68], and shielding the indigenous microbial population from harmful effects during fermentation [63]. Cumulatively, these encouraging impacts are beneficial to improve biohydrogen production.

9.2.2.2 Biomass Washout Issue and Solution Through Cell Immobilization

Biohydrogen fermentation under continuous operation mode is susceptible to biomass washout during severe fermentation environment, short retention time, high organic loss, and shear stress due to stirring/mixing [69]. In the long run, such a condition deteriorates bioreactor performance and reduces productivity. Although the conventional recycling technique purposely maintains an adequate microbial population for hydrogen production, biomass washout is inevitable in short HRT. Hence, cell immobilization is a promising strategy as it offers cell stability and favors continuous

fermentation modes, economical recycling and recovery cost, improved fermentation productivity, and low-cost downstream processing [70].

Karel *et al.* characterized cell immobilization as the physical entrapment of cells occupied in a space with a specific desired catalytic activity that remained to function [71]. Additionally, because biohydrogen production is sensitive to oxygen, cell immobilization can provide an oxygen-free condition. Immobilization is also insusceptible to strain contamination which is critical for an extended period of biohydrogen fermentation under oxygen-free conditions [69]. Literature survey indicated that various supporting materials had been employed to entrap cells for biohydrogen production, including synthetic polymer of polydimethylsiloxane (PDMS) [72], bamboo stems [73], alginate, and polyvinyl alcohol [74]. These studies have demonstrated that cell immobilization is reliable to increase biohydrogen production compared to the control experiment.

9.2.3 Chemical Issues and Their Mitigation Approaches

9.2.3.1 pH Variation and Its Regulation

Reaching an optimum pH regulation and redox conditions is challenging, especially for the continuous biohydrogen generation system. Significant low pH suppressed the metabolic activity of biohydrogen-producing microbes. A pH-dependent dark fermentation with pig manure and glucose as substrates for biohydrogen generation is well-controlled at the targeted pH by varying the organic loading rate [75]. It was reported that sodium hydroxide could be used for controlling pH reduction due to the presence of volatile fatty acid as the byproduct in a dark fermentation [76]. Thus, the production cost allocated for purchasing sodium hydroxide consumption can be saved. Besides, the methanogenic effluent can be recycled to minimize the pH uncertainty and regulation as this effluent exhibited basic pH of 7–8 [77]. Additionally, previous research indicated that using immobilized microbial cells could increase hydrogen production by using medium pH regulation during dark fermentation biohydrogen generation [78]. However, the enhancement of hydrogen production by the cell immobilization is subjected to the reactor configuration improvement.

9.2.3.2 Limiting Nutrient Loading and Optimization

Nutrients such as inorganic compounds, carbon, nitrogen, and phosphate are accountable for cell growth and biohydrogen generation. During the metabolic activity, the substrate that provides carbon for energy will be

converted into biohydrogen. Moreover, nutrient concentration also affects biohydrogen generation, either increasing or decreasing biohydrogen production [55, 79, 80]. An ideal concentration of phosphate and nitrogen sources is critical for the growth of the biohydrogen-producing microbes to enhance hydrogen yield [81, 82].

Logan *et al.* found that high nitrogen and phosphate concentrations can induce ammonia production, leading to the increment of suspension of compounds and CO_2 concentration [83]. These events affect biohydrogen-producing microbe's growth activity, thereby lowering the quantity of hydrogen production [83]. A study observed that when ± 30% phosphate concentration was introduced of the nominal value, the hydrogen production rate plummed to 40% [81], indicating the existence of optimum concentrations to yield better performance.

Besides nitrogen and phosphate, microelements such as iron, nickel, magnesium, and sodium are also critical for biohydrogen fermentation, especially for inducing enzyme secretion in microorganisms, activating enzymes for catalyzing substrates into biohydrogen, and the transportation of biohydrogen out of microorganism systems [84]. The presence of iron ions assists in synthesizing enzymes and encouraging the catalytic activity of hydrogen fermentation. The combination of sulphur and iron can function as a protein transporter which also helps in metabolic alteration of the enzyme hydrogenase. Ferrum propagates the microorganism's growth rate; hence, high substrate consumption and hydrogen production rate can be increased accordingly [85]. However, ferrum outside the optimal value impedes biohydrogen production [86].

Micronutrients such as nickel facilitate electrons in transporting the hydrogenase, catalyzing hydrogen production. Meanwhile, the Ni-Fe co-catalyst hydrogenase can act as an electron donor, rendering substrate reduction to the proton, thus enhancing biohydrogen production by activating the enzymatic function [87, 88]. Magnesium is another micronutrient needed for cell growth, found in microbial cell membranes, which function as co-factors for enzyme synthesis. Studies suggested that magnesium stimulates enzymes catalyzing the metabolic bioconversion [89, 90]. Overall, an optimum amount of limiting nutrients is crucial for microorganism's health and hydrogen fermentation.

9.2.3.3 Inhibitor Secretion and Its Control

Biohydrogen production, microbial growth, and resporulation prevention are depending on, but are not limited to, the initial concentration of the substrate. For a process demanding high efficiency, a higher organic

loading rate is required. However, a higher substrate concentration does not necessarily promise biohydrogen fermentation, which is restricted by the accumulation of volatile fatty acid (VFA), pH alteration, change in hydrogen partial pressure, and dissolved particles in the system. These issues can cause substrate degradation and metabolic disorders upon microorganisms [91–93]. Additionally, a study indicated that ethanol influenced microbial growth rate, while format and acetate influenced biohydrogen production [94]. Therefore, the optimization of substrate concentration and its processing needs to be conducted, which is as critical as removing the inhibitory compounds using cell dialysis or recycling, to name a few.

Furan is an inhibitor produced during substrate pre-treatment. Literature ascertained that compounds derived from furan (catalyzed by enzymes) could influence glycolysis (a fermentation step), destroy DNA integrity, alter metabolic pathways, and reduce cell growth rate [95–97]. Crushing lignin through the pre-treatment step allows the secretion of phenolic compounds, which is detrimental to the cell membrane by increasing its permeability, thus damaging the membrane. This pre-treatment causes seepage of potassium, phosphate, or proteins, disturbing the cell's metabolic process, for instance, cell activity, microbial evolution, and fermentation pathways. As a result, biohydrogen generation was hampered, as documented in several studies [98–100]. These inhibitory compounds can be minimized during the pre-treatment step by applying various biological, physical, chemical, or other detoxification treatments in the hydrolysate, such as enzymatic, evaporative, alkaline, carbon and activated carbon, respectively [101–103]. Lin *et al.* eliminated the inhibitory compounds produced from the dark fermentation process by using sodium borohydride [104]. A study suggested that biohydrogen production can be enhanced by preparing detoxifying agents by mixing activated carbon, chitosan, sludge powder, and sodium alginate with calcium chloride solution [105].

Ammonia is another inhibitor produced during dark fermentation that impedes biohydrogen generation in anaerobic digestion. Ammonia is synthesized by decomposing a nitrogen-rich compound such as protein, urea, nitrate, and food waste. High concentrations of ammonia and free ammonium ions deter biohydrogen production [106–108]. The presence of free ammonia could lead to cell membrane destruction and the combination of free ammonia with a proton to produce ammonium ions which cause intracellular pH variation, followed by the ammonium ion accumulation due to reverse activity of antiporter, thereby constraining microbial metabolic activity [25].

Moreover, high ammonia concentration has also been proven to alter the dark fermentation metabolic pathway that produces soluble metabolites,

reducing biohydrogen production [109]. This study also confirmed that the acclimation of microflora in dark fermentation could also lessen the ammonia inhibition [109]. Several reports have also suggested that several procedures such as microflora acclimation, substrate dilution, pH and temperature control, optimization of C: N ratio, and immobilization by zeolites can lessen ammonia inhibition in anaerobic fermentation [110, 111].

9.2.3.4 Byproduct Formation and Its Exploitation

Another problem arising during biohydrogen fermentation is the production of byproducts causing high acidity effluent on inefficient substrates conversion. The accumulation of mixed soluble acids such as VFA lowers the pH of the medium, affecting the microbial viability, thus diminishing hydrogen production. Several studies reported that only 30% of organic matter was consumed after the acidogenic stage, even under optimal operating conditions [15, 16, 19].

Jiang *et al.* found that the production of VFA at low pH (acid) decreased the biohydrogen production dramatically by 10 times compared to high pH (alkali) because of lesser hydrolytic enzyme activity and the inhibitory nature of acid medium towards microbial viability [112]. Of the total fermentation product, the produced VFA comprises 25% acetic acid, 50% butyric acid, and 15% propionic acid at neutral pH. The commonly generated byproduct during hydrogen production is acetate and butyrate, which the latter produced more at low pH [3]. Studies suggested that recycling waste carbon fractions from acidogenic effluent can improve fuel generation, thus curtailing the consequences of the environmental and economic issue if it is directly discharged to water streams [113–115].

9.2.4 Economic Issues and Ways to Optimize Cost

Operational energy efficiency and economic analysis are the key factors in transforming technology into commercialization. Total capital investment is a critical measure to assess the transformation, which fixed capital and working capital cost must first be considered. Fixed capital costs include the necessity of the selected type and the capacity of the equipment. Meanwhile, the working capital cost needs to be determined based on the manufacturing cost and income, which can be calculated annually. Noting that biohydrogen is acquired through the waste treatment process, the wastewater does not entail further treatment to comply with effluent specifications. Annual income includes the profits from solid waste trade that can be used as fertilizer or livestock bedding,

Table 9.2 Summarization of the prevailing challenges in biohydrogen production and the reported enhancement strategies.

Challenges	Detail of challenges	Enhancement strategies	Ref.
Physical	Achieving an optimum temperature	A shift from mesophilic to thermophilic culture mode	[19]
	Achieving an optimum hydraulic retention time	Shorter HRT inhibited methanogens' growth and their metabolic process	[124]
		Longer HRT could prevent biomass washout	[21]
		Shorten the HRT from 7 to 1 day resulted in a 30-fold enhancement of biohydrogen yield	[23]
	High hydrogen partial pressure	Decreasing hydrogen partial pressure to 20% with 2 hours interval time resulted in improved biohydrogen production efficiency and yield	[125]
		Reducing hydrogen partial pressure during dark fermentation increased biohydrogen production	[31]
	Membrane fouling	Zeolite and activated carbon removed colloids and soluble compounds to lessen fouling on the membrane	[24]
		Carbon nanotubes exhibited high performance to prevent fouling membrane	[64, 126]
		ZnO and TiO_2 improved membrane hydrophilicity and curbed microbial activity	[127, 128]

(*Continued*)

Table 9.2 Summarization of the prevailing challenges in biohydrogen production and the reported enhancement strategies. (*Continued*)

Challenges	Detail of challenges	Enhancement strategies	Ref.
Biological	Slow start-up culture	Inoculating the fermentation media with bio augmented co-culture of *Klebsiella Pneumoniae* (native facultative) *with Clostridium* (an anaerobe bacteria)	[129]
		Bioaugmenting native acidophiles with three acidophilic strains (*Pseudomonas stutzeri, Lysinibacillus fusiformis,* and *B. subtilis*) treating food wastewater in anaerobic sequencing batch reactors	[63]
	Biomass washout	Immobilizing microbes using alginate, polyvinyl alcohol etc.	[74]
		Immobilizing cells using synthetic polymer, polydimethylsiloxane (PDMS) and resulted in an improved biohydrogen generation rate [91]	[72]
		Using bamboo stems as supporting carriers for immobilizing cells	[72]

(*Continued*)

Table 9.2 Summarization of the prevailing challenges in biohydrogen production and the reported enhancement strategies. (*Continued*)

Challenges	Detail of challenges	Enhancement strategies	Ref.
Chemical	Achieving an optimum pH medium	Maintaining pH below six which favors the growth of biohydrogen producing microbes	[130]
		Maximum production of biohydrogen was achieved at a pH of 5.5 and reduced to a pH of 4.5	[131]
		Adjusting pH using potassium hydroxide, sodium hydroxide, calcium hydroxide as buffering agents [103,104]	[132, 133]
	Determining nutrient loading	Applying low nitrogen and phosphate concentrations to prevent biohydrogen degeneration due to a rise in CO_2 concentration, compound dissolution, and ammonia production	[83]
		Introducing iron, sodium, nickel, and magnesium to induce enzyme production, which converts the substrate to biohydrogen	[84, 134]
		Loading iron accelerates the microorganism's growth rate, thus consuming more substrate, increasing substrate oxidation and hydrogen production rate [130]	[85, 135]
		Adding up magnesium stimulates enzymes accountable for bioconversion metabolism	[136]

(*Continued*)

Table 9.2 Summarization of the prevailing challenges in biohydrogen production and the reported enhancement strategies. (*Continued*)

Challenges	Detail of challenges	Enhancement strategies	Ref.
		Combining Ni^{2+}, Fe^{3+}, Mo^{6+} ions in media composition, threefold hydrogen can be produced compared to control	[137]
	Inhibitor production	Using alkali, evaporation, activated carbon, and biocatalysis to eliminate the inhibiting compound	[101, 138, 139]
		In the dark fermentation process, sodium borohydride was applied to eliminate the generated inhibitory compounds	[104]
		Formulating a detoxification agent containing calcium chloride, activated carbon, sodium alginate, powdered sludge, and chitosan increases biohydrogen production	[105]
		Utilizing acclimated microflora substrate dilution, optimized C:N ratio, pH and temperature, to inhibit ammonia production in anaerobic fermentation	[110, 111]
	Unwanted byproduct formation	Reducing HRT and Increasing the organic loading rate	[140]
		Switching operation mode from batch to continuous at the early process	[141]
Economy	High operating cost	Selecting proper substrate and process for biohydrogen fermentation because it highly affects the production cost	[118, 120, 122, 123]

biomethane, biohydrogen, and charges incurred for waste treatment services. The net current value, internal reimbursement rate, and payback time are defined as profit from system operation. The net current value represents the total project cost throughout the process. The internal reimbursement rate is the interest rate at zero net present value, where a more significant internal cost of return is anticipated. Additionally, the payback time is the time required to recover the capital costs invested at the beginning of operation [112, 116, 117].

An economic investigation for biohydrogen production dealing with the mixture of food waste and corn flour in the two-phase fermentation discovered that the production cost was considerably low at $\$0.19/N.m^3$ [118]. As suggested, the profit can be amplified by taking advantage of eliminating waste disposal [118]. Ljunggren *et al.* showed that the use of barley straw waste reduced hydrogen production, which was burdened by the additional cost for maintaining pH, thus increasing production costs to \$583.5/GJ [119]. When potato steam skins were used as substrates, the considerably high capital and nutrient costs reduced the economic value of the produced biohydrogen, as reported by Ljunggren & Zacchi [120]. Meanwhile, when substrates such as sugar beet molasses were used in two-stage dark fermentation and photolysis, the biohydrogen production cost increased significantly, attributed to the dominating expenses of capital and operating cost [121]. In other studies, the cost of a reactor to perform single-stage algal bio photolysis was estimated to be 50 per/m^2; meanwhile, 80% of the total cost was allocated for fixed capital costs [122]. Akkerman *et al.* estimated the cost of hydrogen production at \$15/GJ; thereby, biohydrogen production cost from the photolysis process is in the range of \$10–20 per GJ [123]. Based on the review above, the production cost is also greatly influenced by the type of substrate and processing technique for biohydrogen production. For a quick reference, a summarization of challenges and their mitigation strategies in biohydrogen fermentation is tabulated in Table 9.2.

9.3 Conclusion and Future Direction

High reliance on depleting fossil-based fuel and improper management of solid waste are two main reasons causing the unceasing emissions of greenhouse gases. It remains a serious environmental concern considering the exponential energy demand by the ever-increasing human population and lifestyle. The extraction of biohydrogen from waste through anaerobic fermentation is foreseen to solve the energy

and environmental issues through hydrogen economics by adopting the waste-to-wealth concept. As simple as it sounds, the bioconversion of waste to biohydrogen production through anaerobic digestion remained challenging in terms of the accumulation of inhibitory compounds, a low substrate conversion rate that influences the bio-catalytic pathway, and the marketability of biohydrogen production. Literature suggested that the pre-treatment and combined process, for instance, the employment of two-stage anaerobic digestion, can improve the energy extraction efficiency owing to the concurrent production of hydrogen and methane. Hence more energy from waste materials can be harvested.

Furthermore, the recovery of valuable byproducts accumulated in the effluent during biohydrogen fermentation contributes to the circular economy of biohydrogen production. Moreover, researchers unanimously agreed that an enhanced biomass conversion to biohydrogen could also be realized by applying nanocatalyst during fermentation. The integration of anaerobic digestion and electrochemical reaction in microbial electrolysis cells (MECs) would enhance hydrogen production, given that extra hydrogen can be produced through fermentation and electrochemical activity. Genetic modification on hydrogen-producing microorganisms was also proposed to improve biohydrogen production. Most importantly, the price and efficiency of the fuel that is competitive with the current fossil-based fuel would quicken the transition from technology to commercialization. Research on biohydrogen production, storage, and utilization should be simulated under optimal parameters and configuration near practical conditions, which could also improve the adoption rate of hydrogen fuel into practicality.

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