Critical challenges in biohydrogen production processes from the organic feedstocks

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REVIEW ARTICLE

Critical challenges in biohydrogen production processes from the organic feedstocks

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Abstract

The ever-increasing world energy demand drives the need for new and sustainable renewable fuel to mitigate problems associated with greenhouse gas emissions such as climate change. This helps in the development toward decarbonisation. Thus, in recent years, hydrogen has been seen as a promising candidate in global renewable energy agendas, where the production of biohydrogen gains more attention compared with fossil-based hydrogen. In this review, biohydrogen production using organic waste materials through fermentation, biophotolysis, microbial electrolysis cell and gasification are discussed and analysed from a technological perspective. The main focus herein is to summarise and criticise through bibliometric analysis and put forward the guidelines for the potential future routes of biohydrogen production from biomass and especially organic waste materials. This research review claims that substantial efforts currently and, in the future, should focus on biohydrogen production from integrated technology of processes of (i) dark and photofermentation, (ii) microbial electrolysis cell (MEC) and (iii) gasification of combined different biowastes. Furthermore, bibliometric mapping shows that hydrogen production from biomethanol and the modelling process are growing areas in the biohydrogen research that lead to zero-carbon energy soon.

Keywords Biohydrogen · Fermentation · Bio-photolysis · Biowaste · Waste to energy · Microbial electrolysis cell · Gasification · Climate change

Nomenclature

ATP	Adenosine triphosphate
BOD	Biological oxygen demand
Chl	Chlorophyll *a*+*b*
CCWP	Concentrated cheese whey permeate
COD	Chemical oxygen demand
DF	Dark fermentation
GHG	Greenhouse gas
HRT	Hydraulic retention time
HPR	Hydrogen production rate
HC	Hydrocarbon
H_2SO_4	Sulphuric acid
LCA	Life cycle assessment
MEC	Microbial electrolysis cell
NG	Natural gas
OLR	Organic loading rate
PNSB	Purple non-sulphur bacteria
PF	Photofermentation
SCW	Second cheese whey
SRT	Solid retention time
TS	Total solid
VSS	Volatile suspended solids
VS	Volatile solid
WGSR	Water gas shift reaction
WoS	Web of Science

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1 Introduction

The depletion of fossil-based fuel sources along with their increasing use day by day has created big concerns related to greenhouse gas (GHG) emissions and global warming. Increasing levels of CO_2, which is a patent GHG emission and associated with burning fossil fuel sources, were found

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to exceed 409 ppm [1–3], which is aiding to the global temperature increase [4, 5]. Moreover, growing industrial and economic development of the modern world is also demanding more sources of clean energy for the near future. The increasing gap between the growing energy demand and necessary energy supply due to at the rising human population has sparked a huge interest in new biofuel research as well as production in recent times [6]. Therefore, from the perspective of alternative energy sources, renewable energy sectors like solar, hydro, wind and biofuels like biodiesel, bioethanol and biohydrogen are finding its use in current development agendas across the world. Recently, hydrogen production by water electrolysis has gained global attention as one of the most promising and eco-friendly energy alternatives. H_2 is found to have a high energy content of around 122 kJ/g, about 2.75 times higher than other HC fuels [7, 8]. It also possesses wide versatility in its production as well as its applications ranging from fuel-cells to biofertilisers and biofuels. H_2 produced from biological sources is known as bio-H_2. Hydrogen produces no harmful greenhouse gases upon combustion but only water. Therefore, it is considered one of the energy sources to have the potential to replace part of the conventional fossil-based fuels shortly [9].

As far the production is concerned, fossil fuel is responsible for the majority of hydrogen production, out of which 60% is produced from dedicated primary hydrogen-producing facilities. It is also reported that around 71.27% of hydrogen is produced from natural gas (NG), 27.27% from coal, 0.7% from petroleum and the remaining 0.7% from water electrolysis [10–12]. Notably, the hydrogen production from fossil reformation is neither renewable nor carbon neutral as the production process involves high numbers of GHG footprints [4]. H_2 production is also achieved with water gas shift reaction (WGSR), thermal decomposition, catalytic oxidation, steam gasification, pyrolysis and autothermal reforming [13, 14]. The recent popularity of waste-to-energy studies also creates an impact on research related to hydrogen production utilising waste materials effectively. Biohydrogen is produced from different organic wastes, thereby solving the issue of waste disposal and energy generation at the same time. Organic waste can be defined as the waste materials that are biodegradable and originates from plants or animals which can be broken into CO_2, methane or simple organic molecules [15]. Organic wastes like industrial waste, municipal sewage sludge, solid waste, agricultural residues and poultry waste, manure, have the potential to be used for bioenergy production [16].

However, recent publications suggested further investigations are required on the production of H_2 using organic waste materials. The concept of using waste materials from different biological sources to produce environment-friendly biohydrogen can be potentially helpful to tackle the ongoing environmental challenges, while for all H_2 production processes (NG reforming, biomass and coal gasification, water electrolysis and others), there are requirements for better reliability and operating flexibility, a reduction in the capital costs and a significant enhancement in the plant efficiencies [17]. Herein, we assessed the routes of biohydrogen production derived from different organic waste materials and highlighted the key factors affecting the yield of biohydrogen. Furthermore, through bibliometric mapping, we suggest steps and future guidelines from the gaps in the literature for the optimisation of hydrogen production from organic waste streams. Overall, this critical review is aimed at helping the academics working in the biohydrogen production research area along with the industrial application and roll-out of a zero-carbon economy. It will also focus on themes that face the development and potential transformation of the biohydrogen market and its future.

2 Review methodology

Web of Science (WoS) was utilised herein to obtain the data within the core collection database and then the exported data files; some Boolean operator logic was implemented in the search to find suitable publications and identify evidence gaps in the knowledge and research concerning the biohydrogen topic. A broad timespan of biohydrogen research covering all available year option in the time frame of 1970–2020 is shown in Fig. 1. The bibliometric mapping generated from the WoS core collection is shown in Fig. 1. The overall number of data which was 1539 was exported to the VOSviewer software. Herein, we used the co-occurrence as the type of analysis and all keywords included and the fractional counting method employed. We have direct clusters in Fig. 1 linking specific keywords to general areas such as biohydrogen production. This approach enabled us to visualise the most distinguished keywords in publications in the last 50 years for biohydrogen production. For example, keywords like dark fermentation, water and ethanol production along with lignocellulosic biomass were the most frequently occurring keywords. Other common related keywords to the biohydrogen production are hydrolysis, pyrolysis, gasification, enzymatic hydrolysis, biodiesel production, sludge, microalgae, wastewater, anaerobic digestion, photo-fermentation, glucose, supercritical water and saccharification. Furthermore, the WoS search showed other keywords associated with the production conditions such as pre-treatment, pH, light and temperature. On the other hand, new keywords have been introduced to biohydrogen production recently such as methanol, modelling, storage, fuel-cells, energy recovery, organic waste, bioreactors, light intensity, methanogenesis along with the techno-economic and life cycle assessment (LCA) studies. This implies that areas such as hydrogen production from

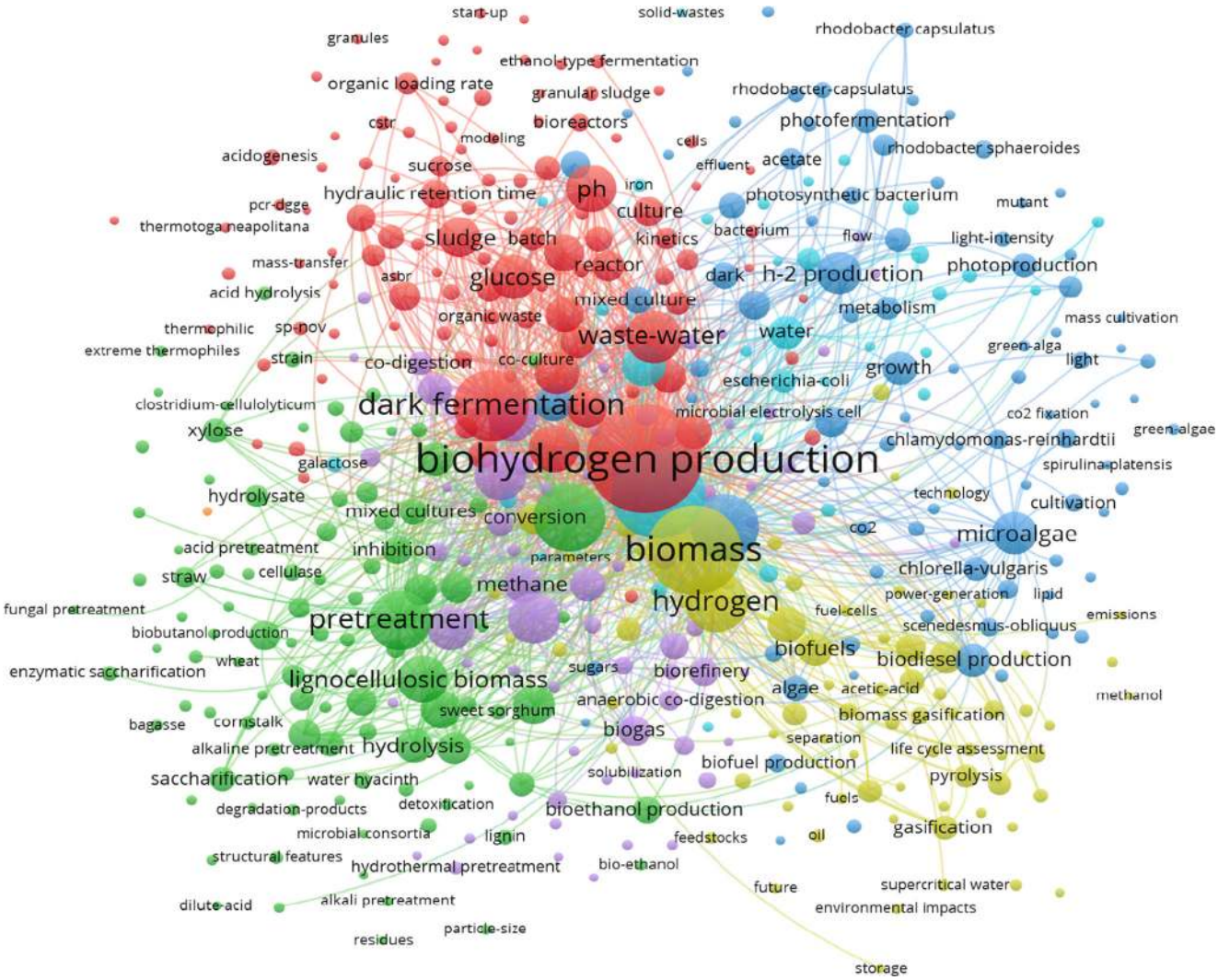

Fig. 1 The bibliometric mapping of biohydrogen production in the last 50 years

methanol need further investigations along with modelling, techno-economic analysis and other research areas.

3 Production of biohydrogen from organic waste through biological methods

Although most of the hydrogen production currently is based on fossil fuels, efforts to produce biohydrogen from different bioresiduals such as wastewater or organic wastes are seen to be increasing [18]. Currently, the most popular, widely discussed and developed processes of biohydrogen production using organic waste material are (a) biofermentation (dark fermentation and photofermentation), (b) biophotolysis (direct and indirect), (c) bioelectrochemical system such as microbial electrolysis cells (MEC) and (d) gasification [19, 20]. Table 1 shows the recent status of the different biohydrogen production processes along with their energy conversion efficiencies. Energy conversion efficiency can be defined as the ratio between the useful output of an energy conversion machine/process and energy input [25]. In this section, these processes of biohydrogen production are discussed. Figure 2 shows the different biological processes involved in biohydrogen production. Biohydrogen production with dark fermentation, MEC and biomass gasification possesses high process efficiency, and biomass is the common feedstock in all of the aforementioned processes. Again, photofermentation and biophotolysis can be seen dependant on solar energy for the production of biohydrogen. Different process parameters are associated with all these processes, which have their own importance. Every process has its certain specification and operating conditions along with advantages and disadvantages which are discussed below.

Table 1 Status of available biohydrogen production technologies

Production process	Feedstock	Maturity	Energy conversion efficiency (%)	[Ref.]
Dark fermentation	Biomass	Long term	4.3	[21]
Photo fermentation	Biomass + sunlight	Long term	5.1	[21]
Bio photolysis	Sunlight + water	Long term	2.7–4.0	[22]
Microbial electrolysis cells	Biomass + electricity	Long term	11.3	[23]
Biomass gasification	Biomass	Commercial	88.1	[24]

3.1 Fermentation

Fermentation can be defined as the process of energy generation involving an endogenous electron acceptor from the oxidation of organic waste materials using a number of different microorganisms. The results of fermentation depend on the applied catalyst (isolated enzyme or microorganism producer) and used organic substrate (mostly carbohydrate or protein), along with the process parameters. The character of the fermentation process can be either aerobic or anaerobic [26]. Fermentation of organic waste materials using microorganisms under anaerobic conditions is a good way to produce H_2 along with other organic alcohols/acids as by-products. Depending on the necessity of light for the microorganisms, the biofermentation can be divided into two types: (a) dark fermentation and (b) photo fermentation. Dark fermentation is the process of fermentation carried out in dark anaerobic conditions, where breakdown of cellulosic organic feedstock results in the production of biological hydrogen along with organic acids and alcohols [27]. Unlike dark fermentation, photofermentation uses photosynthetic bacteria that use sunlight to produce CO_2 and H_2 from organic molecules under anaerobic conditions [28]. For improving the yield of biohydrogen, studies related to the integration of both the two fermentation processes can also be found. Figure 3 shows the two types of biofermentation processes used for H_2 production.

3.1.1 Dark fermentation

Dark fermentation has become one of the well-known technologies for biohydrogen production, which enables the microorganisms to produce H_2 in a dark anaerobic condition [29]. However, with the formation of many by-products, the low H_2 yield on substrates is a major disadvantage. Equations 1 and 2 show the main reactions that are involved in the dark fermentation process of hydrogen production. Equation 1 shows the reaction for H_2 production as a result of the proton reduction by generated electrons from C-source degradation. [NiFe]-hydrogenase and [FeFe]-hydrogenase are generally involved in such process of H_2 formation [30]. A maximum H_2

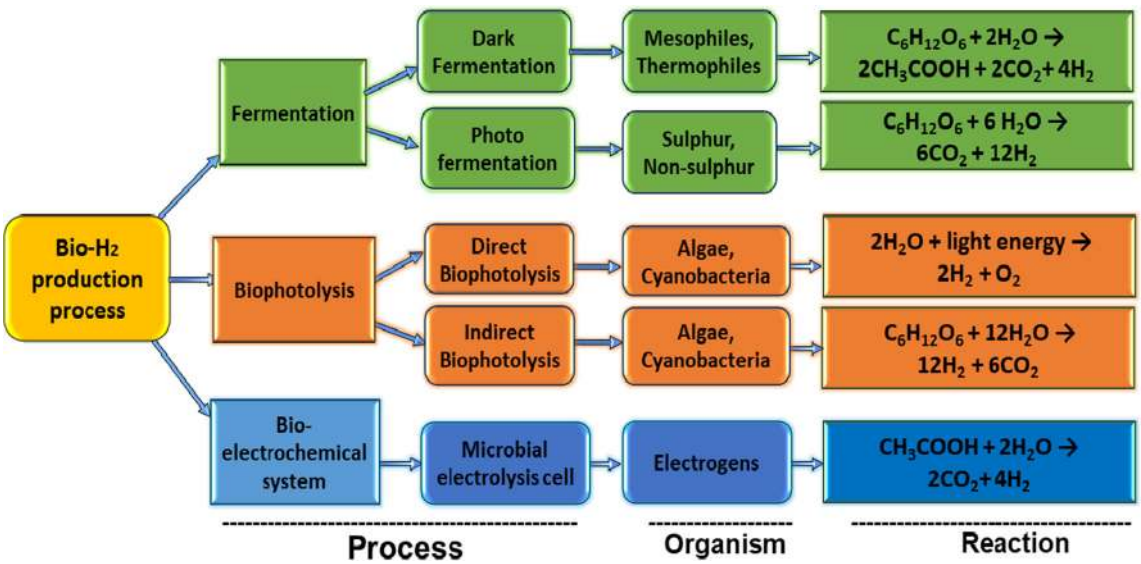

Fig. 2 Overview of the biological biohydrogen production processes

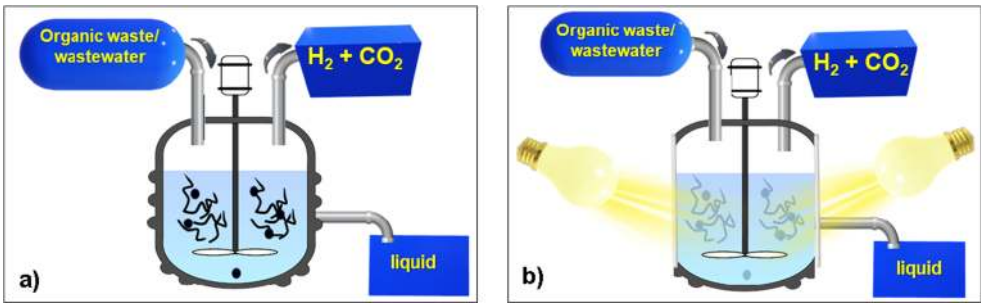

Fig. 3 **a** Dark fermentation and **b** photofermentaion processes during the hydrogen production from organic waste or wastewater

yield of 4 mol H_2/mol glucose can be seen to be achievable in the dark fermentation process practically, though Eq. 2 shows a theoretical yield of 12 mol H_2/mol glucose [31]. Higher yields can be achieved in thermophilic fermentations. This low yield in dark fermentation is mainly happening due to the production of other by-products such as acetic acid, propionic acid and butyric acid. Equation 3 shows the acetic acid pathway, where the reaction of glucose and two water molecules produce acetic acid (CH_3COOH). Similarly, propionic acid can be found to be produced along with acetic acid from glucose, as shown in Eq. 4. Again, Eq. 5 shows the production of butyric acid from glucose reacting with six water molecules [32]. In all the three pathways, CO_2 and H_2 are seen to be produced in different quantities.

$$2H^+ + 2e^- \leftrightarrow H_2 \quad (1)$$

$$C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 12H_2 \quad (2)$$

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2 \quad (3)$$

(Acetic acid pathway)

$$C_6H_{12}O_6 \rightarrow CH_3COOH + CH_3CH_2COOH + CO_2 + H_2 \quad (4)$$

(Propionic acid pathway)

$$C_6H_{12}O_6 + 6H_2O \rightarrow 2CH_3CH_2CH_2COOH + 2CO_2 + 2H_2 \quad (5)$$

(Butyric acid pathway)

Several types of waste with different chemical compositions are seen used as a substrate to produce H_2 in the dark fermentation process. Among those, the most widely used waste includes agricultural wastes (viz. rice/wheat/corn straw, animal manure), various wastewater types (viz. distillery wastewater, cheese whey effluent, palm oil mill effluent), food waste, municipal sewage waste and sewage sludge [33]. The sugar or carbohydrate-rich waste substrates tend to produce more H_2 compared with lipid or protein-rich substrates. A linear correlation between H_2 production and the proportion of carbohydrate-rich waste substrate was also found [34]. Waste like sewage sludge and palm oil mill effluent usually have a low H_2 yield compared with other waste due to the high presence of protein or lipid [33].

The pre-treatment is a crucial step in biohydrogen research. Table 2 shows various studies related to pre-treatment methods, like physical (high temperature, ultrasonication and microwave), mechanical (milling and grinding), enzymatic, radiation and hydrothermal pre-treatment for the improvement of H_2 yield [49–51]. Different types of substrates need different pre-treatment methods, which can enhance the production efficiency of hydrogen. Pre-treatment of dairy manure can be done mainly with three different methods: (a) acid (0.2% w/w HCI solution) treatment, (b) alkali (0.2% w/w NaOH solution) treatment and (c) 2 h infrared oven treatment [33, 35]. In the case of sewage sludge, 15-min boiling at around 100 °C completes the pre-treatment [36]. Pre-treatment of rice straw for hydrogen production was found with boiling at 80–100 °C [37], and in another case, treatment with alkali solution (1% w/w) was found with cellulose hydrolysis after cutting and grinding (2 mm size) [41]. Distillery wastewater was also found to be pre-treated with pH neutralisation, centrifugation and sterilisation [39]. Food waste was found to be pre-treated in many ways. Sieving and 6 h boiling at around 100 °C of food waste hydrolysate for hydrogen production were reported by Han et al. [42]. Kim et al. [43] mentioned pre-treatment of food waste and sludge mixture with 30-min heating (at 120 °C), alkalisation (3 M NaOH) and acidification (3 M HCl). Kitchen mill shredding was also applied as a pre-treatment method to food waste combined with 5% glycerol [44].

The H_2 yield of 1130 mmol/g COD was reported for plain palm oil, while an improvement of 2760 and 1880 mmol/g COD was found for surfactant (Tween 80) and enzyme (Optimase BG) pre-treatment, respectively [52]. Efficient H_2 production with lignocellulosic materials like sugarcane bagasse rice/corn/wheat straw and corn stalk from agricultural waste needs pre-treatment as mentioned in several different studies [53, 54]. An increase in 47.3% of biohydrogen production was seen for pre-treatment of rice husk with a commercial enzyme (Celluclast 1.5 L) compared with that of rice husk without pre-treatment (321 mL H_2/g rice husk) [54]. Similarly, 35% high H_2 yield (155 mL H_2/g VS) was seen in

Table 2 Comparison of biohydrogen production from wastes with the dark fermentation process

Substrate	Pre-treatment process	Microorganism	pH	Temperature (°C)	H_2 yield (mL/g VS)	[Ref.]
Dairy manure	HCl (0.2%) treatment, boiling/infrared radiation	Mixed culture	5.0	36.0 ± 1	31.5	[35]
Sewage sludge	100 °C boiling (for 15 min)	Mixed culture	7.0	37.0	11.2	[36]
Sewage sludge + poplar leaves					20.8	
Sewage sludge + flower waste					32.0	
Sewage sludge + ryegrass					51.0	
Rice straw	80–100 °C boiling	Activated sewage sludge	4.0–5.5	35.0	14.5 + 0.3	[37]
Food waste+ sewage sludge +3% crude glycerol	100 °C heat shock (for 30 min)	Mixed culture	5.5	35.0	179.3	[38]
Distillery wastewater	Neutralisation (to pH 6.7 with KOH), 5000 rpm centrifugation, sterilisation	Mixed culture	5.0	37.0	1.6 ± 0.3*	[39]
Cassava wastewater	Sieving, 95 °C boiling (for 15 mins)	Mixed culture	5.5	37.0	39.8**	[40]
Rice straw	Cutting and grinding (2 mm size), 1.0% alkali pre-treatment, cellulose hydrolysis	*Clostridium pasteurianum*	7.5	37.0 ± 2	2.6*** (47.6 mL/g released sugar)	[41]
Food waste hydrolysate	Sieving, 100 °C boiling (for 6 h)	*A. awamori*, *A. oryzae*	4.0–4.6	37.0	219.9 (39.1 mL/g food waste)	[42]
Food waste + sludge	120 °C heating (for 30 mins), alkalisation (3 M NaOH), acidification (3 M HCl)	-	5.5 ± 0.1	37.0	13.8	[43]
Food waste +5% crude glycerol	Kitchen mill shredding	Mixed culture	5.0–5.5	35.0 ± 1	180.0	[44]
Sugarcane bagasse	H_2SO_4 (2%) in solid-to-liquid and mass ratio 1:15, 121 °C sterilisation (for 1 h)	*Enterobacter aerogenes*	6.8	30.0	1000.0****	[45]
Brewery wastewater	Dilution with distilled water, pH adjustment with HCL and NaOH	*Klebsiella pneumoniae*	5.5	35.0 ± 1	1.7*****	[46]
Glucose	–	*Thermotoga neapolitana*	6.5	70.0	1.7*****	[47]
Wheat straw	Overnight soaking in acetic acid, steam explosion at 190 °C (for 10 min), enzymatic hydrolysis for 72 h	*Caldicellulosiruptor saccharolyticus*	6.5 ± 0.1	70.0	134.0******	[48]

*mL/mL wastewater; **mL/g- COD; ***L/L hydrolysate

****mL/L hydrolysate; *****mol H_2 mol^{-1} glucose; ******mmol H_2/L

the case of cornstalk pre-treated with lime compared with that of the untreated stalk (115 mL H_2/g VS) [55]. Song et al. [56] studied biohydrogen production from an aquatic weed, *Alternanthera philoxeroides*, pre-treated with 1% H_2SO_4 at 135 °C for 15 min, using *Enterobacter aerogenes* ZJU1. The optimum H_2 production was found to increase by 59.9% to reach production of 62.2 mL/g with pre-treatment compared with 38.9 mL/g VS for the raw material, without pre-treatment. That low hydrogen yield may be due to the utilisation of different feedstocks (115 mL H_2/g VS). Shao et al. [57] used dilute acid (1% H_2SO_4)-pre-treated duckweed biomass for H_2 production using dark fermentation. They found a maximum H_2 yield of 169.30 mL/g dry weight under a temperature condition of 35 °C and an initial pH value of 7.0. Acid pre-treatment (0.2% HCl) of dairy manure was also seen improving the H_2 yield by 36%; further 6.8 and 4.5% improvement in H_2 production from dairy manure was reported for base pre-treatment (0.2% NaOH) solution and infrared oven pre-treatment, respectively [35]. Thus, it can be seen that pre-treatment of substrates is highly recommended for good yield of biohydrogen in dark fermentation.

Another important parameter for the dark fermentation biohydrogen yield is the pH environment value. pH level in the dark fermentation process is found to influence the metabolic pathway and microorganism activity of the microorganisms and thereby affect the substrate degradation and production efficiency. The pH levels at the start of operation and during the process were seen carefully maintained in many dark fermentation studies [58–60]. Using dark fermentation of cheese whey wastewater, the highest biohydrogen production was found at pH 5.5 and pH 6.5 for thermophilic and mesophilic conditions, respectively [59]. Xing et al. [35] studied a wide variation in pH between 4.0 and 12.0 for fermentation of dairy manure. At pH 5.0, they found the highest biohydrogen yield of 31.5 mL/g VS. A pH below 4.0 and above 12.0 showed no biohydrogen production.

Hydrogenotrophic methanogens act as one of the major H_2-consuming microorganisms which reduced the H_2 yield by consuming H_2 to produce methane. Therefore, inhibiting the production of hydrogenotrophic methanogens, which acts as an H_2-consuming microorganism, is one of the major steps for dark fermentation. Pre-treatment of inoculum is considered for enriching H_2-producing bacteria and suppressing H_2-consuming methanogens. Since methanogens are strictly anaerobic microorganisms, aeration around the reactor can inhibit the methanogen production and thereby increase the H_2 yield [61]. The impact of pH in the growth of methanogen is another important aspect of biohydrogen yield. It has been reported that methanogens are capable of producing methane by consuming H_2 under an optimal pH range of 7–8 and optimal hydraulic retention time (HRT) of 15–20 days [62]. Kumar et al. [63] attained a hydrogen yield of 29.5 mL/g VS with pH 5.5 and methanogenic inhibitor from mixed microalgae biomass (*Scendesmus* and *Chlorella*).

Production of biohydrogen by dark fermentation is accomplished by various microorganisms that are capable of converting a wide range of organic waste substrates. Based on different living temperatures, these microorganisms are classified as thermophiles (45–65 °C), mesophiles (25–45 °C) and psychrophiles (0–25 °C). The commonly used mesophilic cultures for H_2 production are *Clostridium* and *Enterobacter* (*Clostridium beijerinckii*, *Clostridium butyricum*, *Enterobacter aerogenes* and *Enterobacter asburiae*); while the most reported thermophilic one is *Thermoanaerobium (Thermoanaerobacterium thermosaccharolyticum)* [35]. Again, depending on their growth of metabolism in the presence of oxygen, they are divided as facultative (e.g. *E. cloacae*, *Enterobacter aerogenes*, *Citrobacter intermedius* and *Escherichia coli*) or obligate bacteria (e.g. *C. paraputrificum*, *Ruminococcus albus* and *Clostridium beijerinckii*) [13, 64]. Facultative bacteria are the organisms that make ATP by aerobic respiration (in the presence of oxygen) and are also capable of anaerobic respiration or fermentation (in the absence of oxygen). On the contrary, obligate bacteria are unable to produce ATP (in the absence of oxygen) and cannot live in the presence of oxygen. *Enterobacter* and *Clostridium* are two species of gram-positive bacteria for large-scale production of hydrogen for their ability of fast-growing and forming endospores. Lactic bacteria like *Klebsiella pneumoniae*, *Cellulomonas* and some thermophilic archaea like *Thermotoga neapolitana* and *Caldicellulosiruptor saccharolyticus* were also found showing good results for H_2 production through dark fermentation [65].

HRT (hydraulic retention time) acts as one of the important parameters for proper fermentation of substrate and efficient H_2 production. The stability of the reactor and utilisation efficiency of the feedstock depends on HRT. Santiago et al. [66] found that HRT and solid retention time (SRT) have a great impact on the biohydrogen production and associated subproducts from organic solid waste (OSW) using a dark fermentation process. A 16 h of HRT and 55 h of SRT were found to be the optimum conditions to maximise the biohydrogen production. HRT was found as the main influencing parameter in the whole process. The substrate hydrolysis rate increased with decreasing HRT time. Moreover, substrate hydrolysis-ssolubilisation process time got reduced with an increase in SRT and a decrease in HRT. Fatty acid production was found maximum with long SRT and HRT of 60 h and 48 h, respectively. Lu et al. [67] studied the effects of HRT and concentration of substrate on the HPR (hydrogen production rate) from glucose in a pilot-scale bioreactor of 3 m^3 with three sequential chambers of 1 m^3 each. A HRT of 24 h and substrate concentration of 30 g/L with a maximum HPR of 100.2 mol/m^3-d were found optimal for the reactor.

The production of biohydrogen using dark fermentation of two different cheese deproteinisation diary waste streams SCW (second cheese whey) and CCWP (concentrated cheese whey permeate) was studied by Colombo et al. [68]. With an increasing OLR (organic loading rate), H_2 production was seen increasing to 3.47 NL H_2/d and 5.07 NL H_2/d for SCW and CCWP, respectively. Similarly, organic acid yield was also found higher with increasing OLR (14.6 g/L/d and 12.6 g/L /d for SCW and CCWP, respectively). Table 2 describes different studies of biohydrogen production from wastes using a dark fermentation pathway. It can be seen that combined fermentation of different substrates leads to an increased biohydrogen yield. Moreover, pre-treatment processes such as acid treatment, base treatment, heat treatment and pH neutralisation have shown a significant impact on the yield of biohydrogen. Most of the studies were found to utilise a mixed culture process for good results.

3.1.2 Photofermentation

The production of H_2 with photofermentation involves decomposition of organic acids with the aid of light-dependant, sulphur and non-sulphur purple bacteria. A group of bacteria having the ability to do photosynthesis is known as purple sulphur bacteria. Again, purple non-sulphur bacteria (PNSB), commonly known as photobacteria, are a group of photoheterotrophic bacteria capable of degrading several carbon substrates like carbohydrate, organic matter, biowastes and organic acids for the production of H_2 [69]. Equations 6 and 7 show the reaction involved with the production of H_2 by photofermentive process from glucose and acetic acid, respectively. Oxidation of organic acids, like acetic acid, propionic acid, butyric acid, lactic acid and malic acid, by photofermentive bacteria, produces H_2 and CO_2. Therefore, to obtain a higher H_2 yield, the two-stage dark fermentation process is often followed by a photofermentation process [70]. The energy needed for the growth of microorganisms is gathered from the production of adenosine triphosphate (ATP) using light through photophosphorylation [4]. Batch or continuous photofermentation process can be obtained using an artificial source of light or solar illumination as shown in Fig. 3b.

$$C_6H_{12}O_6 + 6\,H_2O \rightarrow 6\,CO_2 + 12\,H_2 \quad (6)$$

$$2CH_3COOH + 4H_2O \rightarrow 8H_2 + 4CO_2 \quad (7)$$

The photofermentation process offers the possibility of high H_2 production from a wide variety of substrates including wastewaters (such as olive mill wastewater, dairy wastewater, brewery wastewater) and wastes rich in organic acids (such as dark fermentation effluent, agricultural waste after hydrolysis) [33, 71]. The best H_2-producing microorganism for the photofermentation is PNS (purple non-sulphur bacteria), which include the *Rhodobacter* species (*Rhodobacter capsulatus*, *Rhodobacter sphaeroides*, *Rhodovulum palustris* and *Rhodopseudomonas sulfidophilum*) [72]. Some other bacteria used in H_2 production using nitrogenase and ATP production are *Chlorobium vibrioforme*, *Allochromatium vinosum*, *Desulfuromonas acetoxidans*, *Thiocapsa roseopersicina* and *Chloroflexus aurantiacus* [13]. Hydrogenase and nitrogenase are two different enzymes that help these bacteria to produce H_2 from organic acids using solar energy [73]. Nitrogenase are found to be the main enzymes responsible for H_2 production in limited-O_2 conditions. NH_3 is generally produced from N_2 by nitrogenase (in large-scale production), but in absence of N_2, ATP is used along with redundancy by nitrogenase to generate H_2 [13], as shown in Eq. 8.

$$(2H^+ + 2e^- + 4\,ATP \rightarrow H_2 + 4ADP + Pi). \quad (8)$$

Several studies can be found regarding photofermentive H_2 production in recent years. Mirza et al. [74] found a wide range of 148–513 mL H_2/L photofermentive biohydrogen production using raw sugarcane bagasse with the help of PNSB (purple non-sulphur bacteria) isolated from the paddy rice field *Rhodobacter capsulatus*-PK. A maximum yield of 96 mol H_2/mol sugar was achieved with initial pH 7.0 ± 0.2 and 10% (v/v) inoculum size, at a temperature of 30 ± 2.0 °C along with a light intensity of 120–150 W/m^2. The production of 671 mL/L of H_2 from glucose was also found with this process. For cost reduction of temperature control during summer, *Rhodobacter capsulatus*-PK was found as a good candidate for photofermentive bio-H_2production. García-Sánchez et al. [75] used *Rhodopseudomonas pseudopalustris* to produce H_2 by tequila vinasses (VT) photofermentation. Compared with synthetic medium, they found a double H_2 yield with VT. With the replacement of H_2 by N_2 compared with unchanged headspace, three-time growth was seen in *R. pseudopalustris* up to 4.5 g/L, and the H_2 yield also increased to 860 mL H_2/L. Laurinavichene et al. [39] used PNS bacteria and anaerobic saccharolytic consortium to perform sequential dark photofermentation, which resulted in 17.6 L/L of distillery waste of maximum H_2 yield. Machado et al. [76] investigated the influence of milk whey permeate and glucose on the H_2 yield using PNS bacteria *Rhodobacter capsulatus* and *Rhodopseudomonas palustris* through co-culture. The maximum H_2 yield was found to be 287.39 ± 5.75 mmol of H_2/L day. Keskin and Hallenbeck [77] used beet two major sugar mill waste—black strap and beet molasses for biohydrogen production using photofermentation. The H_2 yield found from pure beet sucrose, black strap and beet molasses are 14 H_2/mol sucrose, 8 H_2/mol sucrose and 10.5 mol H_2/mol sucrose, respectively. A comparative study of different parameters involved in photofermetive biohydrogen production process is shown in Table 3. The

Table 3 Comparison of biohydrogen production with photofermentation

Substrate	Pre-treatment process	Microorganism	pH	Temperature (°C)	Light (W/m^2)	H_2 yield	[Ref.]
DF effluent of distillery wastewater	-	*R.capsulatus* B10, *R. sphaeroides* B-3059	7.0	30.0	30.0	3.2 mL/mL wastewater	[39]
Rotten apple batch	Crushing, sieve screening	Mixed culture	7.1	30.5	24.0	112.0 mL/g TS	[78]
Palm oil mill effluent	-	*Rhodopseudomonas palustris*	5.5	30.0 ± 1	55.3	2.3 mL H_2/mL POME	[79]
DF effluent of sugarcane bagasse	Centrifugation, Vacuum filtration	*Rhodopseudomonas* BHU 01	6.8	34.0	8.5	755.0 mL/L hydrolysate	[45]
DF effluent of corn stover	-	Mixed culture	7.0 ± 0.08	30.0	23.7	4.7 m^3/m^3-d	[80]
Sugar beet molasses	Addition of buffer, pH adjustment, sterilisation	*R. sphaeroides* O.U.001	7.5	30.0	114.0	9.4 mol/mol sucrose	[81]
		R. capsulatus YO3				10.6 mol/mol sucrose	
		R. capsulatus DSM 1710				12.7 mol/mol sucrose	
		Rhodopseudomonas palustris DSM 127				19.0 mol/mol sucrose	
Cornstalk pith	Enzyme cellulase hydrolysis (at 50 °C)	Mixed culture	7.0	30.0	15.8	2.6 mol/mol sugar consumed	[82]
Chlorella pyrenoidosa + cassava starch	Acid (1% H_2SO_4) treatment, heating at 135 °C (for 15 min)	*Clostridium butyricum*	7.0 ± 0.1	30.0 ± 1	47.4	388.0 ± 42.1 mL/g VS	[83]
Cellulose	-	*Cellulomonas fimi* ATCC 484, *Rhodopseudomonas palustris* CGA009	-	30.0	40.0	3.8 mol H_2/mol glucose	[84]
Brewery wastewater	Pre-treated with banana peel	*Rhodobacter sphaeroides* 158 DSM	7.4	30.0 ± 2	126.0	408.3 mL H_2 L^{-1}.	[85]
Cornstalk pith	-	*Rhodospirillum rubrum*, *Rhodopseudmonas capsulata*, *Rhodopseudomonas pulastris*, *Rhodobacter sphaeroides and Rhodobacter capsulatus*	7.3 ± 0.5	30.0	15.8	211.9 mL/L-medium	[86]
Agar embedded molasses	-	*Heat-treated hot-spring sludge*	7.4	37.0	39.5	226.2 mL H_2/g TS	[87]
Corn stover powder		*Rhodobacter sphaeroides*, *Rhodospirillum rubrum*, *Rhodobacter capsulatus and Rhodopseudomonas palustris*	6.5	30.0	47.4–55.3	62.3 ± 0.8 mL/g VS	[88]

Table 4 Comparison of biohydrogen production by microalgae and cyanobacteria

Microalgae/cyanobacteria	Production conditions	pH	T (°C)	Light (W/m^2)	H_2 yield	[Ref.]
C. reinhardtii cbn 1–48 (spectral selective activation of PSI)	Tris-acetate-phosphate medium, 5% CO_2, dark anaerobic adaptation	7.2	25.0 ± 2	426.6	40.2 mL/kg DCW	[92]
C. reinhardtii Dang 137^+ (magnesium deprived)	TAP medium	7.7	25.0	34.1	6.0 mmol/L	[93]
Chlorella sp. IOAC707S (phosphorous deprived)	TAP-seawater medium	7.2	28.0	10.7	38.0 mL/L	[94]
Lyngbya sp. (benzoate as a carbon source	Basal medium, 600 mg/l benzoate at late exponential phase	7.4	32.0	31.6	17.1 μmol H_2/g Chl a/h	[95]
Nostoc PCC 7120 Δ*hupW*	BG110 medium, supplied with a mixture of red and white light, altering 100% Ar and Ar/N2 (20/80)	8.0	30.0	18.8	6.2 ml/L/h	[22]
C. reinhardtii (CC124)	Sulphur-free TAP medium	7.7	-	64.0	1.3 ± 0.1 mL/L/h	[96]
C. reinhardtii CC-425 strain (phosphorus and sulphur deprived)	TAP medium, TAP-sulphur	-	-	121.6	0.8 μmol/mg Chl /h	[97]

temperature variation clearly shows that the optimum operating temperature range of photofermentation lies between 28 and 32 °C. Further, the highest H_2 yield with photofermentation can be seen with a neutral pH value (around 7) in most of the cases [89]. Moreover, the light intensity and HRT play a very important role in the H_2 yield in photofermentation. Because of the slow metabolic activity of PNSB in photofermentation, usually longer HRT can be seen compared with dark fermentation [33]. Moreover, light source plays a very important role in the growth of microorganisms as well as the H_2 yield in photofermentation, which can be easily seen in Table 3.

3.2 Biophotolysis

Biophotolysis or water-splitting photosynthesis is the process in which by using oxygenic photosynthetic microorganisms like cyanobacteria and green microalgae, H_2 can be produced with only sunlight and water. For this process, FeFe-hydrogenase is needed for the green microalgae application and heterocystous cyanobacteria nitrogenase finds its use [13]. Biophotolysis H_2 production can be divided into two ways: (a) direct biophotolysis and (b) indirect biophotolysis.

3.2.1 Direct biophotolysis

In the direct biophotolysis, photosynthetic microorganisms like green algae and cyanobacteria absorb 400–700 nm solar radiation for their cell growth [90]. After accepting solar radiation, the microorganisms can evolve hydrogen through nitrogenase or hydrogenase. In direct biophotolysis, water splitting occurs with a light energy of 680 nm wavelength to produce protons, electrons and oxygen as shown in Eq. 9. The electrons derived from Eq. 9 are transferred through PS II and PS I to a potentially sufficient amount for ferredoxin (Fd) reduction. The reduced Fd then is used for the reduction of hydrogenase enzyme NADP+ to NADPH, which is responsible for the production of H_2, as shown in Eq. 10 [13].

$$2H_2O + \text{light energy} \rightarrow O_2 + 4H^+ + 4e^- \quad (9)$$

$$2H^+ + 2Fd(re) \leftrightarrow H_2 + 2Fd(ox) \quad (10)$$

3.2.2 Indirect biophotolysis

Indirect biophotolysis involves a two-step photosynthetic conversion of light energy to carbohydrates as a form of chemical energy. As shown in Eq. 11, in the first step, using light energy O_2 and carbohydrate (starch and glycogen in green algae and cyanobacteria, respectively) are produced [91]. By limiting N_2 during Eq. 10, an increase in carbohydrate yield and reduction in O_2 amount can be achieved, which subsequently is advantageous for high H_2 yield. The second step involves the conversion of carbohydrate to CO_2 and H_2 with light energy under an anaerobic condition with less O_2, as shown in Eq. 12 and Eq.13. [73].

$$6CO_2 + 12H_2O + \text{light energy} \rightarrow C_6H_{12}O_6 + 6O_2. \quad (11)$$

$$C_6H_{12}O_6 + 2H_2O \rightarrow 4H_2 + 2CH_3COOH + 2CO_2. \quad (12)$$

$$2CH_3COOH + 4H_2O + \text{light energy} \rightarrow 8H_2 + 4CO_2 \quad (13)$$

Many recent research studies can be found producing biohydrogen from green algae and cyanobacteria as shown in Table 4. Kossalbayev et al. [98] studied the biohydrogen yield using four different cyanobacteria strains: (a) *Desertifilum* sp. IPPAS B-1220, (b) *Synechocystis* sp. PCC 6803, (c) *Phormidium corium* B-26 and (d) *Synechococcus*

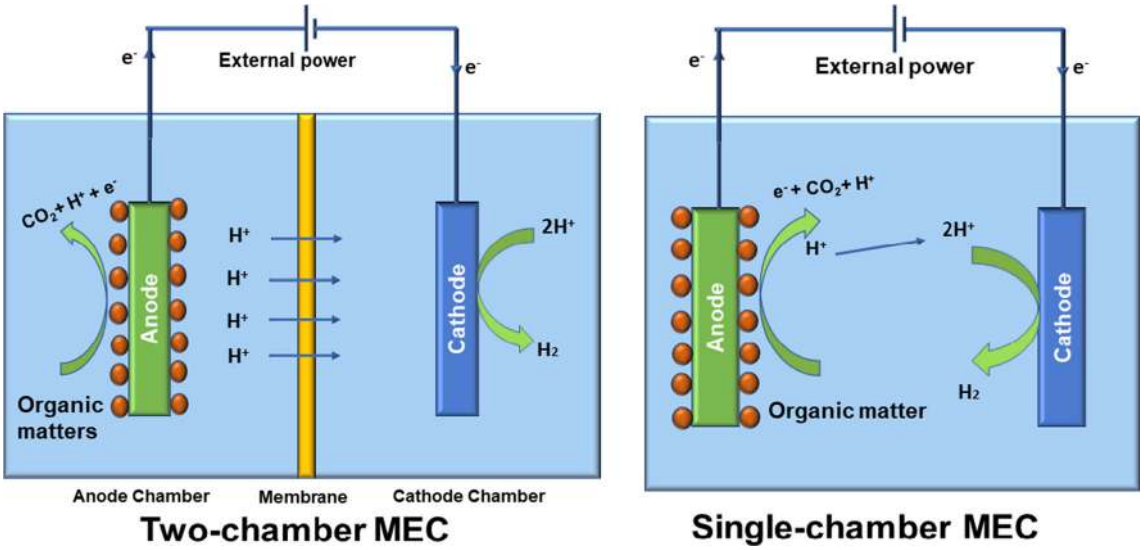

Fig. 4 Schematic diagram of two-chamber and single-chamber MEC (microbial electrolysis cells)

sp. I12. Within 120 dark hours, *Synechocystis* sp. PCC 6803 was seen to have a high H_2 accumulation of 0.037 μmol H_2/mg Chl/h. Again, at 166 h of light incubation, *Desertifilum* sp. IPPAS B-1220 was seen to produce 0.229 μmol H_2/mg Chl/h. Hoshino et al. [92] investigated the H_2 and O_2 yield through the implementation of PS I light in *Chlamydomonas reinhardtii* mutant strains. In a continuous 18 h PS I light supply, H_2 production was seen at 220 dm^3/kg and 176 dm^3/kg for cbn 1–48 (a mutant with a chlorophyll-b deficiency) and VHL^R-S4 (a mutant with high light tolerance), respectively. The highest H_2 production of 366 dm^3/kg was seen in cbn 1–48 under 1.5 h light and dark iteration with PS I-light. Esquível et al. [99] also studied the H_2 yield with biophotolysis by *Chlamydomonas reinhardtii* wild and mutant strains. Kosourov et al. [100] found a maximum of 9.4 μmol/mg chlorophyll/h H_2 yield with a 7.7 pH by using *C. reinhardtii*. Huesemann et al. [101] studied H_2 production using *Plectonema boryanum* (nonheterocystous nitrogen-fixing cyanobacterium) under continuous illumination, where the maximum H_2 production rate was found as 0.18 mL/mg day with a 1 mM initial nitrate concentration under 100 μmol/m^2 light intensity.

3.3 Bioelectrochemical system

Bioelectrochemical system of H_2 production from a wide variety of substrates using microbial electrolysis cells (MEC) is a new technology getting popularity in recent years. MEC technology is also known as biocatalysed electrolysis cells or electrofermentation [13]. As shown in Fig. 4, the MEC system has two electrodes, cathode and anode, which can either be placed in the same single chamber (single-chamber MEC) or be separately placed in two individual chambers (two-chamber MEC). In the two-chamber MEC, to separate the two chambers, commonly a proton exchange membrane is used. Other recently developed membranes include a charge-mosaic membrane, cation/anion exchange membrane and bipolar membrane [102]. In the two-chamber MEC, the anode chamber is filled with the organic wastewater, while the cathode chamber can be filled with different solutions (like moderate acidified water, phosphate-buffered solution, bicarbonate buffers and salt solutions) [103, 104]. The main working process in both the MEC types is the same. Electrons get generated by the oxidation of organic matter in the anode, which are transported to the anode. Then, they are transported to the cathode where upon combining with protons, H_2 gets generated [33].

The initial MEC systems comprised of two chambers avoiding interference of electrodes, which produced high-purity H_2 [105]. MEC acts as an anaerobic system sensitive to oxygen. Equations 14–16 show the production of H_2 using MEC for acetate. In addition to a potential generated by microorganisms (− 0.300 V), MEC needs a small external potential of more than 0.110 V for the production of H_2 [106]. The external power source use of the battery is generally considered, but the use of renewable power generated from solar, wind, MFCs and waste heat can be seen [19, 107].

$$\text{Anode}: CH_3COOH + 2H_2O \rightarrow 2CO_2 + 8e^- + 8H^+ \quad (14)$$

$$\text{Cathode}: 8e^- + 8H^+ \rightarrow 4H_2 \quad (15)$$

$$\text{Overall}: CH_3COOH + 2H_2O \rightarrow 2CO_2 + 4H_2 \quad (16)$$

Many different substrates were found in use for MEC to produce H_2. Some common pure chemical substrates used are butyrate, glucose, acetate and glycol. However, different waste streams like poultry farming wastewater [108, 109], domestic wastewater [105, 110, 111], waste activated sludge [112–114] and industrial wastewater [115, 116] are used in

Table 5 A comparison study of working parameters of MEC

Type of waste	Type of MEC reactor	Temperature (°C)	pH	External voltage (V)	H_2 yield (L/L/d)	[Ref.]
Domestic wastewater	6 two-chamber cassettes (Pilot-scale) MEC	13.5 ± 1.2–21.0 ± 1.2	7.0 ± 0.4 (influent), 6.7 ± 0.2 (effluent)	1.1	0.02 L/L/d	[105]
Swine manure wastewater	Two-chamber MEC	25.0 ± 2	7.0	1.2	5.1*	[108]
Waste activated sludge	Single-chamber MEC	20.0	7.0 ± 0.2	0.6	90.6**	[113]
Effluent from DF sugar beet juice wastewater	Two-chamber MEC	25.0	7.2	0.4	306.0***	[115]
Food processing wastewater (FP)	Single-chamber MEC	30.0	7.3	0.7	0.4	[116]
Chemical industrial wastewater (IN)			6.4		0.6	
Cornstalk wastewater	Two-chamber MEC	25.0 ± 2	7.0	1.0	3.9****	[119]

*mmol/g COD; **mL/g VSS; ***mL/g COD; ****mL/L/d

MEC. Tenca et al. [116] found a higher H_2 yield for methanol-rich industrial wastewater compared with food processing wastewater, but the food processing wastewater was found to have high H_2 selectivity of around 86% compared with that of industrial chemical wastewater. Improvement in the H_2 yield can be seen in many studies with MEC coupled with anaerobic digestion and/or dark fermentation [114, 115, 117, 118]. Huang et al. [117] studied the H_2 production from food waste from anaerobic digestion coupled with the single-chamber MEC. They found 511.02 mL H_2/g VS of the H_2 yield from the continuous AD-MEC process which was much higher than the AD H_2 yield (49.39 mL H_2/g VS). Dhar et al. [115] studied the H_2 yield from sugar beet juice using an integrated MEC dark fermentation process. Overall H_2 yield with the integrated process was found to be 25% of initial chemical oxygen demand (COD) (6 mol H_2/mol $hexose_{added}$) which is much higher than that of dark fermentation alone (13% of initial COD). Li et al. [118] also found a maximum H_2 yield of 387.1 mL H_2/g corn stalk with the integrated dark fermentation MEC process, which was around thrice that from dark fermentation alone with 20 g/L of corn stalk input and 7.0 initial pH value. Lu et al. [114] also found twice H_2 yield with waste activated sludge coupled with MEC (Table 5).

Raw materials, temperature, pH and operating voltage play an important role in determining the H_2 yield in MEC. However, with MEC, it has been noticed that operating temperatures from 0 can be used in producing biohydrogen from wastewater without having significant effects on the yield. An H_2 yield of 0.015 L/L/d was found with domestic wastewater within an operating temperature range of 13 to 21 °C [105]. Heidrich et al. [120] found improvement in exoelectrogen activities with temperature while studying MEC with domestic wastewater within 1–22 °C. Patil et al. [121] also demonstrated operating MEC with wastewater within 0 to 45 °C. Better performance was seen within 10 °C to 20 °C, thereby showing the advantages of MEC over other fermentative biohydrogen production processes. Again, an increasing H_2 yield with increasing external applied voltage was reported in the literature [108, 113].

In MEC, certain microorganisms which are capable of transferring electrons from the chamber to anode are used, known as electrogens. *Shewanella* spp. and *Geobacter* spp. are two popular electrogenic groups, out of which *Shewanella oneidensis* and *Geobacter sulfurreducens* are the most discussed species [122]. *Acetobacterium woodii*, *Ochrobactrum anthropic*, *Sphingomonas strain DJ*, *Rhodopseudomonas palustris* and *Rhodoferax ferrireducens* are some other exoelectrogenic species reported in recent studies [33, 122–124]. Rago et al. [125] found a high H_2 yield (2.6 L $H_2/L_{REACTOR}$/d) with alkaline MEC, using *Alkalibacter* sp. as exoelectrogen.

4 Biohydrogen production through gasification

Gasification of biowaste is another way of producing bio-H_2. In gasification, syngas (a mixture of CO, CO_2, H_2 and CH_4) and several by-products (tar, char, light HCs) are produced by partial oxidation of organic materials at high temperature and pressure [126]. Even though gasification is not a biological process, it is effective for organic waste conversion to hydrogen. The concentration of H_2 produced during gasification can be improved by optimisation of operating parameters. Equations 17–23 show the main reactions involved during gasification.

$$2C + O2 \rightarrow 2CO \quad (17)$$

$$C + O2 \rightarrow CO_2 \quad (18)$$

$$C + H_2O \rightarrow CO + H_2 \quad (19)$$

$$C + CO_2 \rightarrow 2CO \quad (20)$$

$$C + 2H_2 \rightarrow CH_4 \quad (21)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (22)$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad (23)$$

Gasification of different types of waste materials like sewage sludge, municipal solid waste, agricultural and forest biomass, animal manure and food waste has been seen as a popular technology to produce hydrogen [33]. Prasertcharoensuk et al. [127] studied the effect of parameters on hydrogen production through lignocellulosic biomass waste gasification. H_2 content in the syngas was found increasing up to 67 mol% with pyrolysis temperature higher than 800 °C and 0.5–1 cm^3 particle size. Su et al. [128] studied the effects of temperature (400–450 °C), food additive ($NaHCO_3$, NaCl and NaOH) and reaction time (20–60 min) on the supercritical water gasification of food waste. They found a maximum H_2 yield of 12.73 mol/kg with NaOH as a catalytic agent. Zhang et al. [129] found 28.9% H_2 content from food waste with an anaerobic digestion and gasification integrated process. Chang et al. [130] found a maximum of 29.72 g H_2/kg substrate and 19.78 g H_2/kg substrate H_2 yield with bagasse gasification and waste mushroom gasification, respectively. Shie et al. [131] studied plasma gasification of lignocellulosic municipal solid waste for H_2 production. The effect of different factors like biomass type, reaction temperature, feed size, catalyst type and SB (steam-to-biomass) ratio on the H_2 production in a steam gasification process is discussed by Parthasarathy and Narayanan [132]. Nanda et al. [133] studied supercritical water gasification of different agro-food residues and fruit wastes like a banana peel, *Aloe vera* rind, lemon peel, coconut shell, sugarcane bagasse, pineapple peel and orange peel. During the production of biodiesel, glycerol is produced in large quantities as a by-product. Recently, Osman et al. used glycerol along with the alumina foil waste using photocatalysis to produce a steady state of 4.2 millimole H_2 g/TiO_2 hr., which is a promising result of multifunctional cheap photocatalytic materials for the production of green biohydrogen [134].

5 Challenges with biohydrogen production through biological methods

Several studies have been made so far for enhancing the economic feasibility of the H_2 production process via biological methods. Although these processes have different advantages, there are many key challenges also which need to be addressed in future studies [4, 13, 33]. Table 6 describes the different advantages and challenges associated with these processes. As shown in Table 6, the biohydrogen production processes vary from process to process. The maximum yield of H_2 production was found to be 14.2 ± 0.2 mL/g VSS, and H_2 production rate was 0.13 mL/g VSS h [135]. It was found that for photofermentation, the maximum H_2 yield was 642 ± 22 mL, and the maximum H_2 production rate 77.78 mL/L/h, with an initial pH of 7 [136]. In another case, the effect of adding corn stalk enzymatic hydrolysate H_2 yield was found to increase up to 1287.06 mL H_2/g TOC, and the maximum H_2 production rate was found to be 10.23 mL/h [137]. Kossalbayev et al. [98] found a maximum H_2 yield of 0.348 μmol H_2/mg Chl/h with *Desertifilum* sp. IPPAS B-1220. Moreover, energy conversion efficiency with biophotolysis was found to be around 2.4–4% [22]. Jayabalan et al. [138] found a maximum H_2 production rate of 4.38 ± 0.11 mmol/L/D from the sugar industry wastewater using MEC. A H_2 production rate of 3.48 L/L/d and an H_2 yield of 511.02 mL H_2 g^{-1} VS was reported from food waste anaerobic digestion coupled with MEC [117].

Water electrolysis is another way of producing hydrogen from water using electricity. To produce 1 kg H_2, around 9 L

Table 6 Advantages and challenges with biohydrogen production with biological methods

H_2 production processes	Advantages	Challenges
Dark fermentation	➢ The utilisation of a diverse, wide variety of different wastes. ➢ H_2 production rate is high. ➢ Reactor configuration is simple.	➢ Separation of H_2 needed from CO_2+H_2 mixture after production. ➢ BOD level in the effluent is high. ➢ Pre-treatment is necessary for lignocellulosic waste.
Photofermentation	➢ High COD removal rate. ➢ High H_2 yield.	➢ An external source of light is required ➢ H_2 production rate is low. ➢ The need for low light conversion efficiency. ➢ Not suitable for other wastes except VFA-rich waste.
Biophotolysis	➢ Use of renewable energy. ➢ High light H_2 conversion efficiency (microalgae with FeFe hydrogenase).	➢ A customized photobioreactor is required. ➢ H_2 yield is low ➢ External light source is required.
MEC	➢ H_2 yield is high. ➢ High COD removal rate. ➢ Suitable working under room temperature.	➢ H_2 production rate is low. ➢ The need for external voltage. ➢ A catalyst is needed for the electrode.

of water is needed and 8 kg of O_2 occurs as a by-product in this process. The hydrogen produced with water electrolysis has a purity of 99.99 vol% (strongly depending on the type of electrolysis (AEL, PEM, etc.)) [139]. Yuzer et al. [140] found a maximum hydrogen production rate of 11.4 mmol/h with the use of a bipolar membrane. They found the highest energy efficiency of 82% and an exergy efficiency of 68% with the anion exchange membrane. Chakik et al. [141] found a maximum efficiency of 99.13% with a production rate of 2.34 mL/min using a $Zn_{95}\%Cr_5\%$ electrode in 20 g/L NaOH solution at 0.45 A, 5 V. Kovač et al. [142] studied H_2 production with a rate of 1.138 g/h from the electrolysis of alkaline water using solar energy.

Bio-H_2 production through the biological methods, for instance, dark fermentation, can produce H_2 without light along with in photofermentation, and photosynthetic bacteria can use a wide range of spectral energy. However, the energy conversion efficiency, in general, is low with 4.3 and 5.11% for dark and photofermentaion processes, respectively [21]. The major challenges herein are the low bio-H_2 production rate and yield and the high cost of the raw feedstocks; thus, using organic waste materials helps to address this issue.

Overall, hydrogen can be produced from various sources, with potential supply from renewable electricity, nuclear power and lignocellulosic biomass. However, it is currently dominated by using fossil-based fuels. From biomass sources, H_2 production comes mainly from anaerobic digestion, fermentation or gasification routes. While the former route is mature, it only processes specific feedstocks (food waste, sewage sludge and crops waste). While fermentation can utilise and process the non-edible cellulosic part of lignocellulosic biomass, gasification can process the whole portion of the biomass, but the technology is still not fully mature worldwide. H_2 production mostly comes from natural gas and coal, while during its production globally, a greenhouse gas in the form of CO_2 is released which is equivalent to the combined generated annual CO_2 emissions of the UK and Indonesia with an energy consumption of 275 million tonnes of oil equivalent (2% of total worldwide energy demand) [10]. Thus, carbon capture and storage (CCS) is crucial when producing H_2 from fossil-based fuels along with maximising our way of producing H_2 from clean electricity. Currently, the International Energy Agency (IEA) reported that the technical potential of producing hydrogen from renewable electricity is expensive. However, it is expected to decrease by 30% by 2030 due to the scaling up of H_2 production along with progress in renewables technology that comes with a reduction in the costing. Three major technologies could benefit from that: electrolysers (splitting water using electricity to produce H_2), fuel cells and refuelling equipment. With the progress in solar photovoltaic and wind renewable energy technologies along with batteries, renewable electricity could provide both low-carbon electricity and low-carbon H_2, as well as using electrolysis, which accounts for only 2% of the global hydrogen production now. Economically, H_2 production from natural gas is the cheapest method in most of the countries around the world, such as in the Middle East which costs (1$/kg H_2). On the other hand, electrolysis cost is 10–40$/MWh along with full load hours of 3000–6000, so it can compete with natural gas coupled with CCSU (carbon capture storage and utilisation). Interestingly, countries that import natural gas and have available sources of renewables or nuclear power could easily find electrolysis as an attractive option. However, the production of H_2-based fuel using hydrogen as a feedstock is not economically feasible at the moment.

Overall, electrolysis is a promising route where the efficiency of the electrolyser ranges from 60 to 80%, while for other green hydrogen routes such as dark fermentation, photofermentation, biophotolysis and microbial electrolysis cells, their energy conversion efficiencies are low which are 4.3, 5.11, 4.0 and 11.3%, respectively [21–23]. This is as a result of the complex structure of the biomass that requires complicated processing procedures during the production of green bio-H_2. Also, finding the cheap feedstock of biomass is crucial herein. For instance, to meet the theoretical H_2 production demand in the USA, which is 60 MtH_2, this would require nearly 100% of its biomass resources. However, by employing PV or wind power, only 1% or 6% will be required [143]. The factors that affect the costing of H_2 production from electrolysis are the cost for the electricity, capital expenditure requirements, conversion efficiency and annual operating hours.

6 Conclusion

For the future of the zero-carbon economy, biohydrogen is considered a promising candidate for fossil fuel replacement due to its zero-carbon emission. This review study provides a brief critical technological discussion and analysis of the processes that are used in biohydrogen production from organic biowastes along with the factors responsible for the efficient H_2 yield. Herein, raw materials, processing and production techniques and environmental influences of biohydrogen production have been reviewed. Wide varieties of biowaste materials, such as wastewaters, forest and agricultural residues, food wastes and municipal and sewage wastes, have been utilised in biohydrogen production. Regarding the high H_2 yield and feedstock availability, dark fermentation, photofermentation and gasification showed clear promising results. The combined fermentation processes also have shown promising results in different studies. Pre-treatment of the substrate, pH, temperature and hydraulic retention time (HRT) are crucial factors in regulating the optimum biohydrogen production route. The MEC method showed promising results with a good yield of biohydrogen using

waste feedstock under low-temperature conditions. However, a large-scale production with these processes is still challenging. The need for future studies addressing more variants of microorganisms and waste varieties is highly observed. It is the authors' thought that the integration of more than one production process along with different biomass waste streams is required along with modelling to allow better processing for biohydrogen production. This would help alleviate issues concerned with fossil-based fuel, while also promoting environmental benefit as in the production of biohydrogen from sustainable waste materials and consequently working toward the zero-carbon economy.

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