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Biohydrogen From Waste Feedstocks – Materials, Methods and Recent Developments

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Abstract

Hydrogen synthesis from waste materials needs to be cost effective and environment friendly. Thermal and steam reforming processes need gas conditioning and also release carbon dioxide. Biological pathways for hydrogen synthesis are gaining importance due to their mild operating conditions (temperature and pressure). Methods namely dark and photo fermentations photocatalysis, and electrolysis (microbial) are employed for biohydrogen synthesis. Various low cost materials like kitchen waste, activated waste sludge, municipal waste, and waste from various industries can be used as feedstocks. Investigations for biohydrogen are aimed at optimizing operating conditions, microorganism selection, mode of operation, and pre-treatment of raw material. Microalgae contain chlorophyll and have high efficiency for photosynthetic activity. They are capable of synthesizing and accumulating large quantities of biomass. They are used for hydrogen synthesis through photofermentation. Also, they are used as a feedstock for synthesis of biofuel and biogas. Microalgal biomass as feedstock for biohydrogen synthesis has advantages such as high growth rate, excellent carbon dioxide capacity, less water requirement, high carbohydrate contain, and easy cultivation. Disadvantages include low biomass concentration, high water content, and high capital cost. Recent investigations indicate that enzyme stability and hydrolytic efficiency can be increased by using genetic engineering, electric biohydrogenation, and nanomaterials.

Keywords Photofermentation · Dark fermentation · Microorganisms · Substrates · Feedstocks · Yield

1 Introduction

Growth of any nation is indicated by the energy consumed per capita. If the energy used is derived from fossil fuel, it can also indicate depletion of natural resources. Additionally, if the fuel synthesized is liquid or gas with considerable environmental footprints, the growth may lead to environmental degradation with health effects which can be acute and chronic. Synthesis of fuel by sustainable methods is becoming the buzz word across the globe among the scientists. Utilization of waste materials for fuel synthesis can serve the purpose of waste minimization also. Plastic waste is the gift of modern-day development towards production of lighter equipment, spare parts, and vehicles. Plastic bags are popular but nonbiodegradable. The plastic waste can be utilized effectively as composite and also can be used as raw material for synthesis of liquid fuel [1, 2]. Bioethanol generation from waste feedstock is another alternative being explored by the investigators for green energy [3]. Aerobic and anaerobic composting methods are generally utilized for minimization of solid wate. Anaerobic pathways lead to biogas generation [4–6]. Food waste can be converted into ethanol like products. Solid waste including hazardous and biomedical waste can be converted into liquid fuel depending on its composition [7–9]. More than 85% of the fuel requirement in the world is fulfilled by fossil fuel derived energy [10]. Hydrogen is considered as the fuel of next generation that can be used for industrial and vehicle fuel requirements. Depleting resources of fossil fuel highlight importance of green energy [11]. Hydrogen has energy content of 122 kJ/g [12]. The requirement of hydrogen is increasing by 12% every year across the world [12]. Thermal and steam reforming processes need gas conditioning and also release carbon dioxide. In electrolysis, 80% cost goes into electrical energy. Microalgae as a feedstock is

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being explored for biohydrogen. Also, they can be utilized for synthesize biohydrogen through photofermentation [13, 14]. It is promising fuel for the future considering technical, economical, and commercial aspects of other hydrogen synthesis pathways [15].

The cost of biohydrogen production is approximately 2.13 dollars for synthesis via direct biophotolysis, 1.42 dollars via indirect photosynthesis, and 7.61 dollars via fermentation [16]. Green hydrogen made by electrodialysis using renewable sources like solar or wind energy currently costs Rs. 600 to 700 or 7.17 dollars to 8.48 dollars [17]. The cost of hydrogen is decided based on the cost of the electrolyser, the cost of storage, and the cost of electricity. Biohydrogen from biomass can be produced via decentralized generation units with low capacities which can reduce transportation cost. Comparatively, setting up the solar or wind power generation unit at multiple location with decentralized generation can be costlier. Considering that in country like India, where 500 million tons of agricultural residues is produced every year, waste minimization is one of the environmental problems [17]. The biohydrogen synthesis from biomass has edge over hydrogen production via electrodialysis even with renewable energy sources. Steam reforming technology for hydrogen production has disadvantages like low energy efficiency, thermodynamic constraints, and high number of stages [18]. Solar and wind energy for steam reforming is one of the alternatives that is being explored to increase its sustainability. The biohydrogen from biomass, in long run, can be competitive alternative. According to the European biogas commission, the biohydrogen cost ranges from EUR 1.15 to EUR 9.65/kg, and hydrogen production by electrolysis (green hydrogen) fluctuates between EUR 2.51 and EUR 11.94/kg [19]. Both, green and synthetic algae can be used for biohydrogen synthesis. Some ecological concern needs to be addressed while synthesizing or modifying algae for better properties [20–22]. Various types of contactor equipments can be used for biohydrogen synthesis via different mechanisms. Upflow fixed bed anaerobic reactors, horizontal and vertical stirred tank reactors, hybrid anaerobic activated sludge and rotating biological contactor (AnAS-RBC) reactor, anaerobic fluidized bed reactors, and fed batch reactors are utilized for biohydrogen synthesis [23–29]. The molar yield of hydrogen during fermentation can be increasing by reducing carbon dioxide [30]. In photo fermentation, the bacteria absorb the light energy and convert the organic matter into hydrogen and carbon dioxide under anaerobic conditions. Nitrogenase is a key enzyme in the process [31, 32]. There is need to focus on research to address the concerns regarding energy conversion efficiency and economy [33].

Modern research on biohydrogen production is aimed at intensification of the synthesis methods by using modern tools. Machine learning and Artificial intelligence are being explored for modeling of the process [34–38]. Artificial intelligence models and algorithms greatly contribute to hydrogen production, storage, and transportation [39–42]. Investigations are also reported on various pre-treatment technologies for the source materials for enhancing digestion and hydrogen generation in dark fermentation [43–46]. The high butyric acid to acetic acid ratio and low propionic acid concertation is desired form better hydrogen generation efficiency in anaerobic digestion [47]. Methods namely dark fermentation, direct biophotolysis, indirect biophotolysis, and photofermentation can be used for biohydrogen generation from microalgae [48–51]. Biohydrogen can be synthesized from algae by using biophotolysis and fermentation [52].

Sustainable solution for hydrogen generation can be "use of mild processes involving microorganism." This article contains the sources of biohydrogen, its synthesis, and application-oriented research. Advantages of hydrogen as a fuel are summarized in Fig. 1. Biohydrogen can be synthesized from large number of sources, most of which are waste feedstocks. Various feedstocks for biohydrogen are depicted in Fig. 2.

2 Sources

Feedstocks and inoculum sources from literature are summarized in Table 1. Water can be split to obtain hydrogen. Industrial wastewater has been very attractive option for hydrogen generation [10]. Industrial wastewater from sugar, palm oil, and beverage industry can be used for hydrogen synthesis. Anaerobic digestion produces hydrogen as a product. Agro-wastewater can also be used for production of hydrogen [12]. Photofermentation and dark fermentation can be employed to generated hydrogen. In Nigeria, cassava is important economic crop with the production of 41 million metric tons. Wastewater obtained after cassava pressing is high in organic content and hence good candidate for hydrogen generation. Biomass containing pig manure, cocoa mucilage, and coffee mucilage has also been explored for hydrogen [53]. In a country like Columbia, which is largest coffee manufacturing place, coffee mucilage is very attractive alternative for hydrogen generation. Household and restaurant food waste can also be utilized for hydrogen [54]. Acclimatized and non-acclimatized food waste substrates can also be utilized. Rosman et al. used palm oil mill effluent for biohydrogen synthesis [55]. The effluent contains water (90%) and organic matter, and hence, it can be used as a substrate for fermentation process for biohydrogen production. Cocoa residue has enormous potential for obtaining biofuels [56]. Cheese whey, cheese processing wastewater can also be used for hydrogen generation [57]. Dark fermentation for compost and other waste was found to be

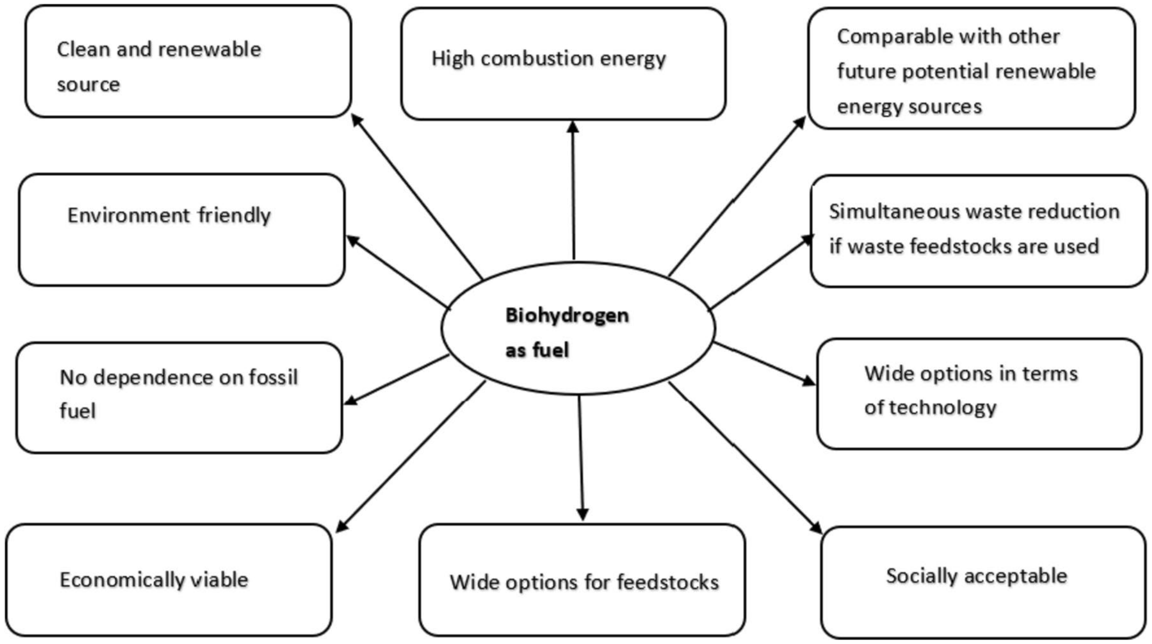

Fig. 1 Advantages of biohydrogen

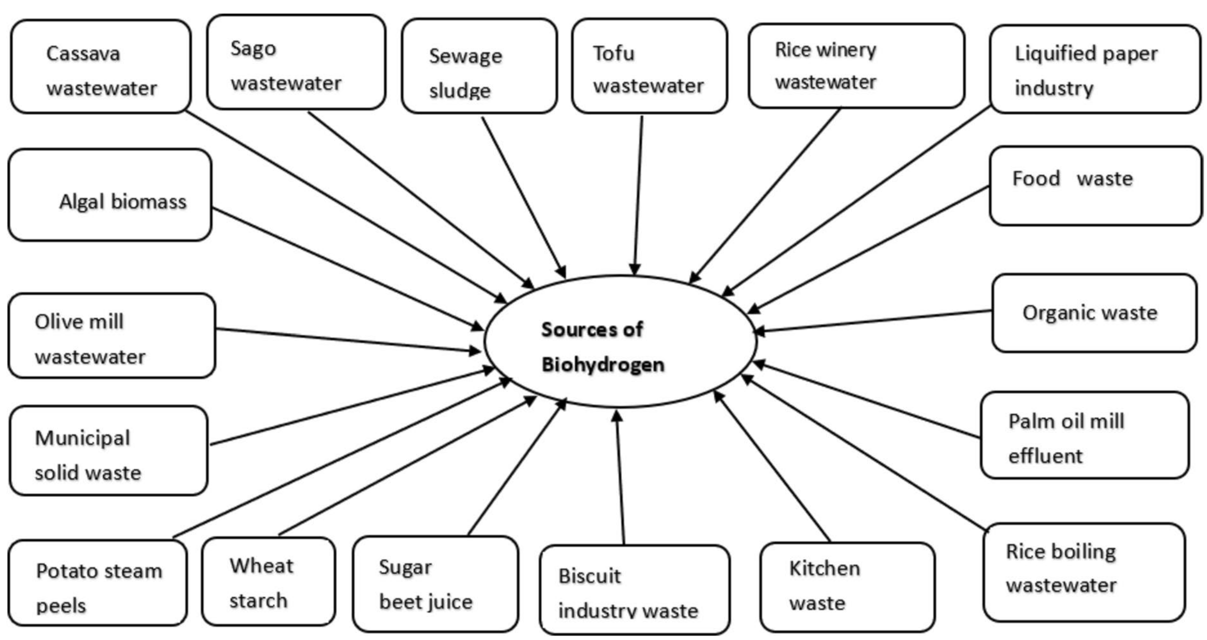

Fig. 2 Waste feedstocks for biohydrogen

suitable for hydrogen synthesis [58]. Anaerobically digested sludge can also be used for hydrogen generation with pure cultures [59–61]. In their investigation involving dark fermentation, Cieciura-Włoch and Borowski used substrate containing sugar beet pulp (SBP), sugar beet leaves (SBL), sugar beet stillage (SBS), stillage (RS), maize silage (MS), fruit and vegetable waste (FVW), kitchen waste (KW), and slaughterhouse waste (SHW) [62]. Dairy wastewater is also explored for hydrogen generation [63]. It contains lipids, protein, and polysaccharides. Sugar, amino acid, and fatty acid are produced after hydrolysis of this waste. After acidogenesis, these are converted into volatile fatty acids which are further degraded to carbon dioxide and hydrogen by acetogens. pH management plays an important role in

Table 1 Sources, equipment, and hydrogen yield for various waste feedstocks

Waste source	Inoculum source	Contact equipment/methods	Highlight	Hydrogen yield/rate/glucose concentration	Optimum HRT/reaction time/capacity
Cassava wastewater [73]	Facultative pond sludge derived from swine wastewater treatment	Anaerobic fluidized bed reactor		1.91 mol H2/mol glucose	2 h
Sago wastewater [74]	E. aerogenes broth	Batch fermentation (Serum bottles)	Acid pre-treatment for complex sugars	Glucose 9.138 g/L, hydrogen 1.7 g/L	
Sewage Sludge [75]		Bioreactor (750-ml working volume) for anaerobic fermentation	The seed without addition of pure hydrogen producer	Maximum hydrogen production 2489 mL/m^3H_2	24 h contact time
Liquefied paper industry biomass [77]	Ameliorate microbial	500-ml beaker, sonicator	Splitting of complex biomass by sonication effected in 4 to 5 times more hydrogen production	17 mL/g VS	Digestion time 384 h
Food waste [79]	An activated aerobic sludge from wastewater treatment plant	3-L glass fermenter	Use of butyric acid to increase tolerance of microorganisms	Hydrogen production rate maximum 5.4 LH_2L/d	9 h batch period and (i.e., 4 HRT) of continuous operation
Organic waste [80]	Compost from Municipal solid waste (MSW) containing methanogenic bacteria	Bioreactor	The sorption catalytic process for purification from carbon dioxide	The synthesized gas had 93 to 98% hydrogen	Hydrogen capacity of reformer 43 L/h
Palm oil mill effluent [81]	Sludge of palm oil mill effluent and cow rumen	Anaerobic batch reactor/circulating bed reactor (CBR) with 5 L volume	Optimum biohydrogen at pH 5.5 to 6.5	15 to 16% hydrogen in synthesized gas	The flushing N2 1 L/min for 24 h, continue to operate for 72 h by biogas
Rice boiling wastewater (RBW) [84]	The activated sludge of the municipal wastewater	500-ml glass bottle	Optimum pH 6.2	s 3.30 mol H2/mol glucose	12 to 36 h contact time
Biscuit industry waste [85]	Microbial isolates from various industrial wastes (dairy, sugar and food)	3 L fermenter	A cyclic heat shock and acid treatment for microorganism for enrichment	0.87 mol H2/mol glucose	16 days
Food wastes [88]	The seed sludge	Serum bottle 160 ml	2-level factorial design study	120 mL/g CHO, maximum hydrogen production rate of 35.69 mL/h	
Sugar beet juice [99]	Mixed culture	Batch reactor		1.7 mol H2/mol hexose, 60% H2 content in gas	
Potato starch [100]	Mixed culture	Batch reactor		0.59 mol/mol starch	
Wheat starch [101]	Mixed culture	Continuous stirred tank reactor		0.83 mol/mol starch d, 50% hydrogen in gas	
Food waste [102]	Mixed culture	Dark fermentation		1.8 mol/mol hexose, 55% hydrogen in gas	
Molasses [103]	E.aerogenes	Dark fermentation		1.5 mol/mol sucrose	
Kitchen waste [104]	Mixed culture	Inclined plug flow reactor continuous		72 cm^3 H2/g VS, 46% hydrogen in gas	

Table 1 (continued)

Waste source	Inoculum source	Contact equipment/methods	Highlight	Hydrogen yield/rate/glucose concentration	Optimum HRT/reaction time/capacity
Organic municipal solid waste [105]	Mixed cultures	CSTR Semi-continuous		55% hydrogen in gas	Hydrogen productivity 5.7 dm^3 H2/dm^3/d
Synthetic food waste (rice, vegetables, meat 30 g COD/dm^3 [106]	Anaerobic sludge from UASB treating cassava wastewater	Batch two-stage		55 cm^3 H2/g VS	
Raw cassava starch [107]	Facultative anaerobic	Batch		1.44 mol H2/mol	
Potato steam peels [108]	Mixed culture	Batch		3,8 mol H2/mol glucose, hydrogen productivity 12.5 mmol H2/dm^3h	

biohydrogen production [64]. In their investigation, Chaudhari et al. studied impact of pH on anaerobic synthesis of bio hydrogen from rice, meat, tofu, egg, noodles bones, potato, and other vegetables [64]. Reyna-Gomez et al. investigated fruit peel wastes namely waste of melon, papaya, and pineapple for hydrogen production [65]. For inoculums, they experimented with two sludge's namely aerobic sludge of municipal waste water and granular anaerobic sludge obtained from distillery wastewater. Biophotolysis and dark fermentation approaches can be used to produce biohydrogen from waste. Dark fermentation is preferred due to higher production rates, ability to produce hydrogen in absence of light and availability of source materials [66]. Fruit waste can be heated from 60 to 80 °C to kill the microbiota from the substrate [67]. Such heat treatment for fruit waste was used for hydrogen synthesis by Pascualone et al. [67]. Two stage hydrothermophilic-mesophilic method was experimented by Abreu et al. for biohydrogen production for garden and fruit waste co-fermentation [68]. Seengenyoung et al. used palm oil effluent as a substrate for biohydrogen synthesis [69]. The effluent was treated with acid and alkali before its utilization. They obtained seed microflora for biohydrogen synthesis from the anaerobic sludge under thermophilic conditions [69]. The effect of sodium ion and ammonia on the biohydrogen synthesis was investigated by Lee et al. [70]. Gasification of the mixed plastic waste was explored for hydrogen synthesis by Lan and Yao [71]. Han et al. carried out batch and continuous experiments to study the synthesis of biohydrogen from food waste with solid liquid ratio of 10%. They used commercial glucoamylase for glucose release in waste food hydrolysate [72]. This glucose is used as a substrate for hydrogen synthesis. Food waste, cassava waste, sewage, and paper industry wastes are among the most widely explored materials for hydrogen production [72–77]. Aerobic and anaerobic sludges and their microbial isolates are utilized as inoculum sources [78–82]. The equipment capacity used for investigation range from 100-ml beaker to 5-L reactor or fermenter [83–88]. Many studies, surveys, and reviews suggest the wide scope for research on biohydrogen production from different sources [89–93]. The storage of hydrogen is still an issue that needs to be addressed. Various aspects of renewable energies need to be assessed and lifecycle studies to explore the most efficient use of feedstocks needs to be reviewed [94–97]. Three important technologies for hydrogen are biological fermentation, thermochemical gasification, and microbial electrolysis cell [97]. Integration of various technologies and feedstocks is also being explored for better and efficient processing for hydrogen synthesis [98]. The aspects of biohydrogen synthesis like the feed stocks, microorganisms, equipment, and yield are widely reported in various review articles [99–102]. As various innovative approaches and methodologies or combinations of the same are explored by the investigators, there are needs to keep the research community updated. Facultative and anaerobic microorganisms have also yielded good results for waste feedstocks [103–108]. Feedstock sources are depicted in Fig. 2. Microalgae contain chlorophyll and have high efficiency for photosynthetic activity. They are capable of synthesizing and accumulating large quantities of biomass [69]. They are used as a feedstock for synthesis of biofuel and biogas. Microalgal biomass as feedstock for biohydrogen synthesis has advantages such as high growth rate, excellent carbon dioxide capacity, less water requirement, high carbohydrate contain, and easy cultivation. Disadvantages include low biomass concentration, high water content, and high capital cost [13–15]. Microalgae are used for hydrogen synthesis through photofermentation and photobiolysis.

3 Methodology

The approaches for biohydrogen synthesis from waste include (a) water splitting by synthetic algae, (b) dark fermentation, and (c) photo fermentation. Green algae for synthesis of biohydrogen are being widely explored by investigators [20]. The algae can be modified or synthesized by applying the genetic modifications for faster growth and attractive properties for synthesis of various compounds [21]. The synthetic algae are effective for synthesis of various products, although there are some ecological risks, that needs to be addressed as it involves genetic modifications [22].

The photobiological hydrogen generation can be oxygenic and non-oxygenic (Fig. 3) [32]. Microalgae and cyanobacteria are involved in oxygenic hydrogen synthesis. In this process termed as direct photo biophotolysis, hydrogen is produced during photoautotrophic growth (Fig. 4). Water is an electron donor; carbon dioxide is the carbon source in the presence of sunlight. Nitrogenase is a key enzyme in the process involving filamentous cyanobacteria. There are two modes involving vegetative and heterocyst cells. This process is also termed as indirect biophotolysis (Fig. 5). In vegetative growth mode, carbon dioxide is fixed into carbohydrate with water as an electron donor in the presence of light. In second mode involving heterocyst, the carbohydrates are converted (oxidized) into adenosine triphosphate (ATP). The electrons generated during oxidation are excited by light and traveled through electron accepter proteins to the final accepter. Finally, the final electron accepter, ferredoxin, transfers the electron to nitrogenase to catalyze hydrogen production from protons and electrons [32]. The hydrogen, in the case of microalgae, is produced during photoautotrophic growth, where carbon dioxide is the carbon source, water is an electron donor, and light is the source of energy. In this direct biophotolysis in microalgae, hydrogenase enzyme catalyzes the hydrogen generation.

Purple non-sulphur bacteria (PNSB) is used in non-oxygenic hydrogen synthesis by photobiophotolysis

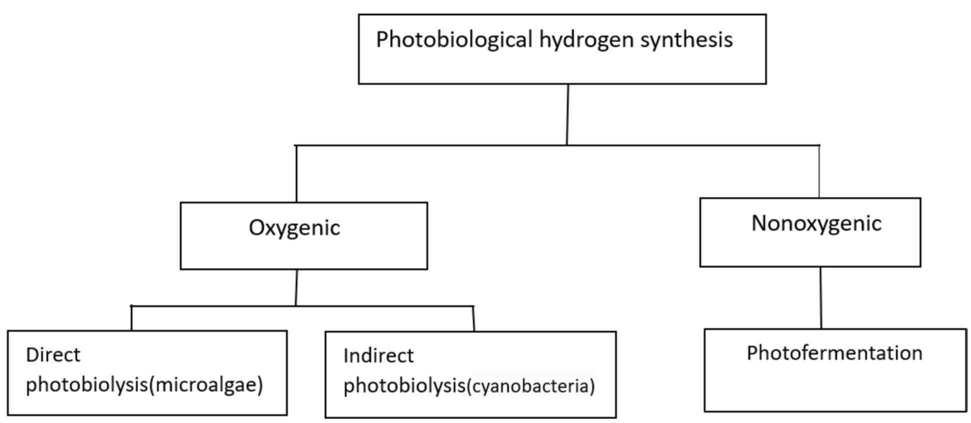

Fig. 3 Photobiological hydrogen synthesis

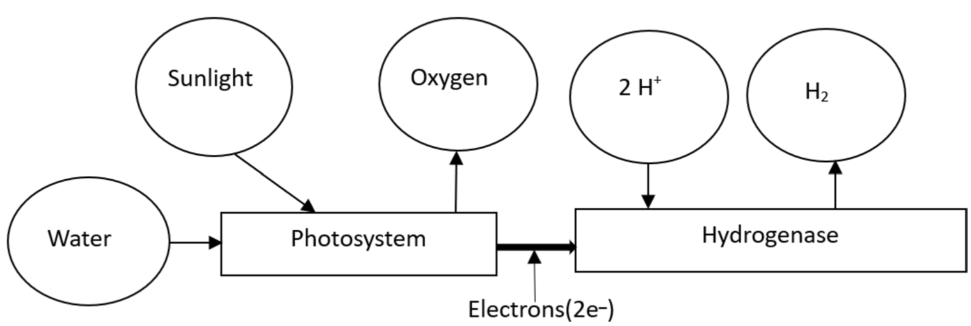

Fig. 4 Direct photobiolysis

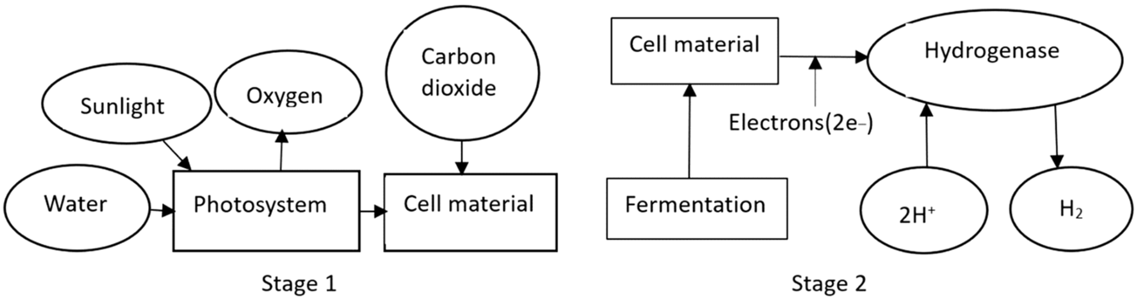

Fig. 5 Indirect photobiolysis

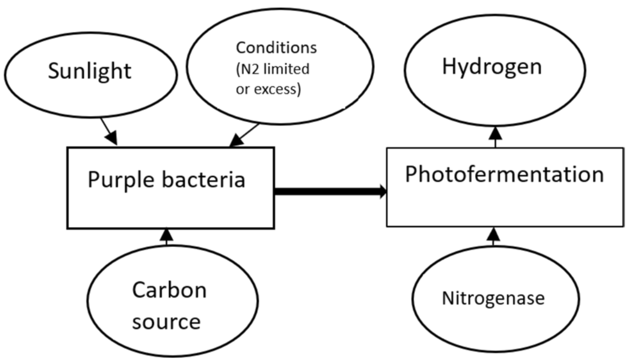

Fig. 6 Photofermentation

(photofermentation). They utilize sunlight for heterotrophic growth, during which hydrogen is generated. Nitrogenase facilitates the hydrogen generation from electrons generated during substrate oxidation [32]. Figure 6 depicts photofermentation mechanism.

Dark fermentation for biowaste is widely studied by investigators since it is efficient and effective method of hydrogen generation (Fig. 7) [58, 61]. For dark fermentation, stirred bioreactor can be used that can be placed in water bath to maintain thermophilic conditions. Mineral containing trace elements and essential nutrients is fed to the bioreactor inoculated with slurry. The operation was fed batch and carbon source used was glucose. This method can be used prominently for easily biodegradable waste [58]. Composite waste containing food waste, potato pulp, and cattle manure is good source of feedstock for hydrogen synthesis [60]. These wastes have interactive effect on hydrogen production. In their methodology for hydrogen synthesis from composite feed, Liu et al. separated coarse gravels, egg shells, plastic etc. from the wastes [60]. Food and potato waste were homogenized and stored at sub-zero temperature by them. The digester sludge from methane plant for cattle manure treatment was used. Similar method was used by Cieciura-Włoch and Borowski and Moreno-Davila et al. [62, 63]. Moreno-Davila et al. employed a method involving biofilm formation [63]. For this, they used dried stems of O. imbricate as a substrate. Anaerobic biofilm was formed on the substrate in a plastic up flow reactor and then mixed culture was introduced. Chaudhari et al., in their work, synthesized biohydrogen from a mix of food, noodle, and rice waste [64]. They mixed the waste with equal amount of sludge in an anaerobic digester. They conducted two set of experiments, one with pH management to pH 7 every 12 h and other with pH management, every 24 h. For measurement of hydrogen produced, the reactors were connected with 3% sodium hydroxide solution. The result indicated that the frequency of pH management has significant effect on hydrogen synthesis. In their methodology for synthesis of biogas from fruit peel waste, Reyna-Gomez et al. employed a Plackett–Burman (PB) experimental design to obtain influence of temperature, inoculums sources, and the C/N ratio on hydrogen production [65]. They carried out experiments with three values of each parameter resulting in 18 combinations of operating parameters.

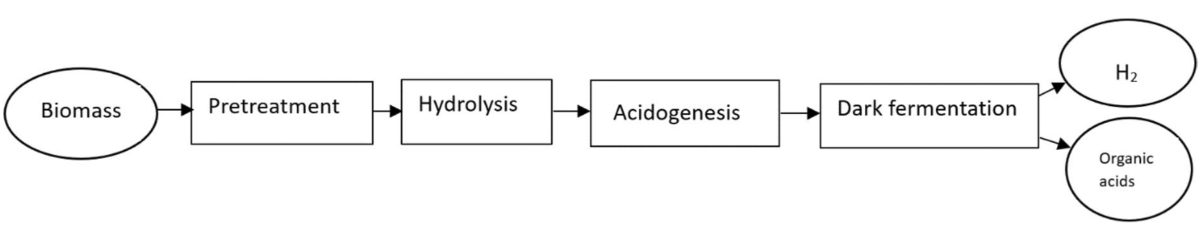

Fig. 7 Dark fermentation

Granular activated sludge at 37 °C and C/N ratio of 30 were optimum conditions for hydrogen synthesis [65].

According to Anzola-Rojas et al., for synthesis of hydrogen by anaerobic mechanism using sucrose-based wastewater, C/N ratio affects the biogas production. This can be attributed to continuous decrease of specific organic loading rate as biomass accumulates in the bed, resulting in rapid increase in hydrogen consuming microorganisms [23]. According to the investigation, optimum C/N ratio was 140. At lower C/N ratio (nitrogen in excess), the energy is utilized for cell growth and assimilation and hydrogen consuming microorganisms proliferate. With increase in C/N ratio (lesser nitrogen content), cell growth reduces due to lesser nutrient availability, resulting in increased hydrogen release rate [23].

Spherical nature of the granules distributes the microorganisms in layers resulting in more efficiency. Synergetic effect of nutritive balance and buffer capacity results in optimum C/N ratio. Studies indicate that prevention of hydrogen loss through acetogenesis on fermentation is the thrust area in the hydrogen synthesis [66]. Manipulating the temperature, agitation, and pH conditions is one way of reducing oxygen loss through acetogenesis [66]. Carbon dioxide capture at the headspace can be considered as one of the methods to prevent hydrogen loss to acetogenesis. Due to generation of acetic acid from carbon dioxide and hydrogen, considerable amount of hydrogen is lost. Chemical scavengers like potassium hydroxide can be used for reducing carbon dioxide concentration in the headspace. An investigation by Park et al. indicated that by using this method, there was 77% reduction in hydrogen loss [30]. The ratio of 7 to 10 was found to be optimum in the literature [66]. In their attempt to synthesize biohydrogen from fruit waste, Pascualone et al. pre-treated the inoculum to avoid methanogenic microorganisms. For the pre-treatment, the incolumn was heated to 100 °C on a water bath and then incubated at 35 °C for 1 day [67]. Plunger displacement system for biogas measurement and chromatographic method for biogas analysis can be used. Food waste and garden waste in different proportions were tested for biohydrogen production by Abreu et al. [68]. For studying effect of sodium and ammonia ions on hydrogen synthesis from fruit waste, Lee et al. prepared synthetic medium using different mineral salts [70]. Two stage bioprocess study was proposed by Han et al. [72]. They used commercial glucoamylase to glucose release in waste food hydrolysate. This glucose is used as a substrate for hydrogen synthesis. Microalgae are used for hydrogen synthesis through photo fermentation. Algae can also be used as a feedstock for biohydrogen production by dark fermentation. Dark fermentation is light independent and involves heterotrophic fermentation [14].

Different modes of contacting patterns for hydrogen synthesis include batch reactors, continuous stirred tank reactors (CSTR), and fed batch reactors [23–29]. The CSTRs are most preferred reactors for hydrogen synthesis due to lower resistance to mass transfer due to even suspension of microbial culture [29]. Waste and inoculum sources, equipments, and hydrogen yield reported in literature is tabulated in Table 1.

4 Results and Inferences

The experiment with composite waste by Liu et al. indicated that food waste and cattle manure have synergic effect for hydrogen generation. It was also inferred that acetic-butyric metabolic pathway play major role in the synthesis of hydrogen [60]. The hydrogen yielding fermentations are butyric acid fermentation and mixed acid fermentation. Lactic acid bacteria (LAB) are found in almost all the bacterial communities in dark fermentation. LAB may reduce hydrogen yield due to substrate competitions for lactic acid and ethanol fermentation instead of hydrogen fermentation [43]. Interaction between LAB and clostridia has positive effect on hydrogen yield due to hydrogen production from lactate by many clostridial species and symbiotic interactions. According to Sikora et al., pH can be important factor in bacterial growth [43]. Taheri et al. investigated the effect of sodium hydroxide on hydrogen generation from sludge with acetate-butyrate [44]. They used potassium hydroxide for pre-treatment in acetate-ethanol pathway. Their study indicated a lower hydrogen yield with acetate–ethanol pathway. Kim et al. investigated effect of various pre-treatment technologies on biohydrogen synthesis by anaerobic digestion [45]. They found that alkalization and ultrasonication combination was most effective for pre-treatment of the sludge. Thermal treatment of anaerobic sludge is dominated by spore forming microorganisms (Clostridia species) which are responsible for hydrogen generation during butyric acid production [46, 47]. Hence, in biohydrogen production by anaerobic digestion, the high butyric acid to acetic acid ratio indicates a higher high efficiency of biohydrogen synthesis [46, 47].

In case of cattle manures as feedstock, for increase in hydrogen production, hydrolysis of lignocelluloses needs to be enhanced. Experiments conducted by Cieciura-Włoch and Borowski indicated that the substrate with plant origin is suitable for the biohydrogen generation [62]. Heat pretreatment and acidic pH deactivates the hydrogen consuming methanogens. The research on pH management frequency indicated that the initialization time was affected by the temperature changes. Increase in temperature from 37 to 55 °C resulted in early starts of bio hydrogen production in food waste reactor. This effect is not significant for noodle waste reactor and rice waste reactor. The biohydrogen production for all three waste reactors, namely food waste, noodle waste, and rice waste ceased after 72 h [64]. Carbon dioxide capture with 80% sodium hydroxide was found to be an effective method for increasing hydrogen production with biomass to microorganism ratio of 7 by Abug and Oh [66]. The experiments by Pascualone et al. on fruit waste and vermicompost yielded a biogas with 21 to 46% hydrogen and rest carbon dioxide [67]. The absence of methane indicated the effectiveness of heat shock to kill the methane forming bacteria. Hydrogen yield increased by 1.5 to 2.5 times due to heat treatment. Maximum yield for garden waste and food waste combination was obtained for 90:10 ratio and corresponding yields were 46 to 47% [67]. In a similar investigation, for hydrogen synthesis with chemical pre-treatment of substrate, a gas containing 55–60% hydrogen was obtained. The pH value of 5.5 and 60 °C temperature were optimum conditions in this case with increase in yield by 51% compared to non-treated substrate [69]. The sodium and ammonia ions have significant effect on hydrogen production. Low carbon-to-nitrogen ratio and high salt content in the medium favor hydrogen production [70]. The hydrogen production rate of 8.02 mmol/(hL) was obtained using food waste hydrolysate as substrate in CSTR compared to 5.31 for glucose as substrate [72]. Also, hydrogen yield in a continuous mode was 20% more than in batch mode.

5 Discussion on Recent Investigations

Microalgae are generally viewed as photosynthetic. Certain algae can grow fast in enclosed container when provided with hydrocarbon sources [51]. The ability of some photosynthetic algae to shift to a dark aerobic fermentation results in bioactive compounds in short span of time and little water requirement [51].

For hydrogen generation from microalgae, direct biophotolysis, indirect biophotolysis, and photofermentation technics can be used [48–51, 109]. Enzyme stability and hydrolytic efficiency can be increased by using genetic engineering, electric biohydrogenation, and nanomaterials. Recent investigations include pre-treatment of biomass for better yield, fermentation conditions, equipment, and substrate resource [110–115]. The biohydrogen synthesis from algae is viable alternative. There is need to address the bottlenecks in this method to make it economically feasible [74]. The synthesis of oxygen during photobiolysis of algae causes inhibitory effect. In indirect biophotolysis, algae produce hydrogen in sulphur free environment. The absence of sulphur can cause inactivation of photosystem and reduction in oxygen consumption leading to anaerobic conditions. Sulphur deprivation thus leads to hydrogenase activity. However, after some time, the algae need to go to normal photobiolysis to rejuvenate. This affects continuity of hydrogen production [52]. Dark fermentation is promising process but limited due to low yield and difficulties in purification of product gas [116–120]. Photo fermentative method for biohydrogen can be improved for light transfer efficiency and enzyme activity. Genetic engineering can be handy in this development [121]. Addition of iron can increase the rate of photofermentation [122]. Biological and nano-based methods can be used for increasing the hydrogen production [123–126]. In case of microbial electrolysis cell, modification in cathode material can improve hydrogen generation [127]. Biohydrogen production in thermophilic bioreactors can be increased by using low graphene oxide [128]. Lactate-driven fermentation has been explored for finding optimum production conditions. Neutral pH and low total solid favor lactate-driven fermentation [129]. Nanoparticles can be used as an additive to enhance biohydrogen production due to their large surface area, high catalytic activity, and intra-cellular electron transfer ability[130]. Microbial electrolysis is a new technology for biohydrogen synthesis (Fig. 8). Named also as biocatalysed electrolysis and electrofermentation, this system utilizes different substrates in electrolysis. The wastewater in the anode chamber is oxidized, and the generated electrons are transferred to anode. These electrons travel to the cathode and generate hydrogen after combining with protons [33].

Modern approach includes application of artificial intelligence for data driven models that allows quick response approximation for fermentative biohydrogen production. It also accounts for non-linear interactions between input variables [131]. Artificial intelligence can play a major role in predicting parameters, safety requirements, and hydrogen storage [34, 35]. Many machine learning algorithms are used for modeling of complex and non-linear relationships among various parameters [36–38]. It helps in predicting process parameters and microbial population [36, 37]. Artificial intelligence along with machine learning can play important role in transportation, safety, and synthesis through application of algorithms and models such as support vector regression, fuzzy logic, and artificial neural network [38]. Energy forecasting, fault detection, and diagnosis by using artificial intelligence can improve the maintenance aspect of biohydrogen facilities [39]. A supply chain system can be optimized by using AI (40). In the process involving microbial electrolysis, AI and ML can be used to optimize the process by predicting various parameters. AI and ML can also be utilized to manage demand supply of hydrogen [41, 42]. Figure 9 depicts the role AI and ML can play in Biohydrogen Synthesis and its application.

The dark fermentation process can be improved by fruit peel-based crude enzymes [132]. Dark fermentation can also be improved by adding olive leaf extract-based iron oxide nanoparticles and microalgae extract-based iron oxide nanoparticles. These can cause 41% and 28% increases in hydrogen production, respectively [133].

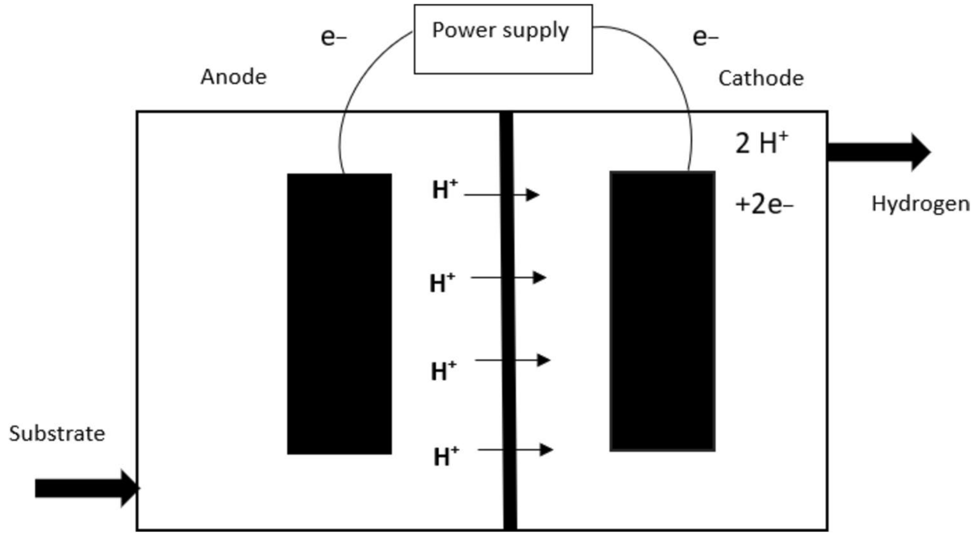

Fig. 8 Microbial electrolysis cell

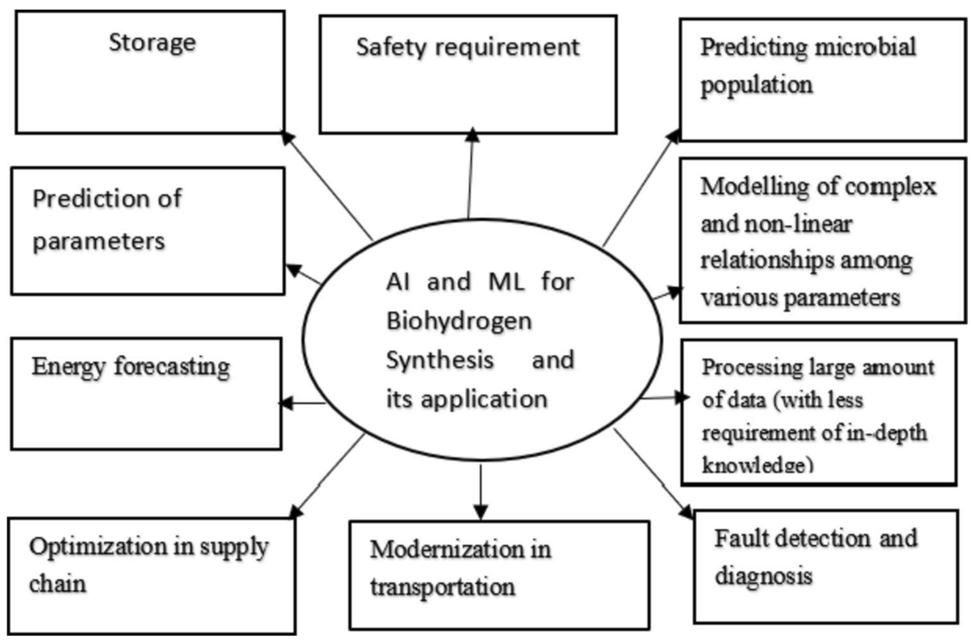

Fig. 9 AI and ML for biohydrogen synthesis and its application

Nickel ferrite can also be used for increasing effectiveness of lignocellulosic hydrolysate-based synthesis [134]. Many investigations are reported on application of organic and inorganic nanoparticles for enhancing hydrogen synthesis [135–138]. Biohydrogen purification is also important aspect in biohydrogen synthesis. Adsorption on different adsorbents for efficient purification is being explored. Waste-derived activated carbon impregnated with metal oxides was very effective with more than 90% purity of hydrogen [139]. In catalytic synthesis, it is important to synthesize effective catalyst in terms of light absorption [140]. Combination of the operational strategies can yield excellent results for biohydrogen production in future [141]. Hydrogen yield from waste sludge can be improved by using various pre-treatment methods like sonication, centrifugation, and chemical addition [142].

6 Advantages and Challenges

Dark fermentation has advantages like simple reactor configuration, high hydrogen production, and ability to utilize wide variety of source. The cost-effective separation of hydrogen from carbon dioxide is a challenge for the investigators. Photofermentation has disadvantage of low hydrogen generation and it is suitable for volatile fatty acid (VFA) rich waste [33]. The biophotolysis needs specialized photobioreactor. The hydrogen generation by MEC is limited by

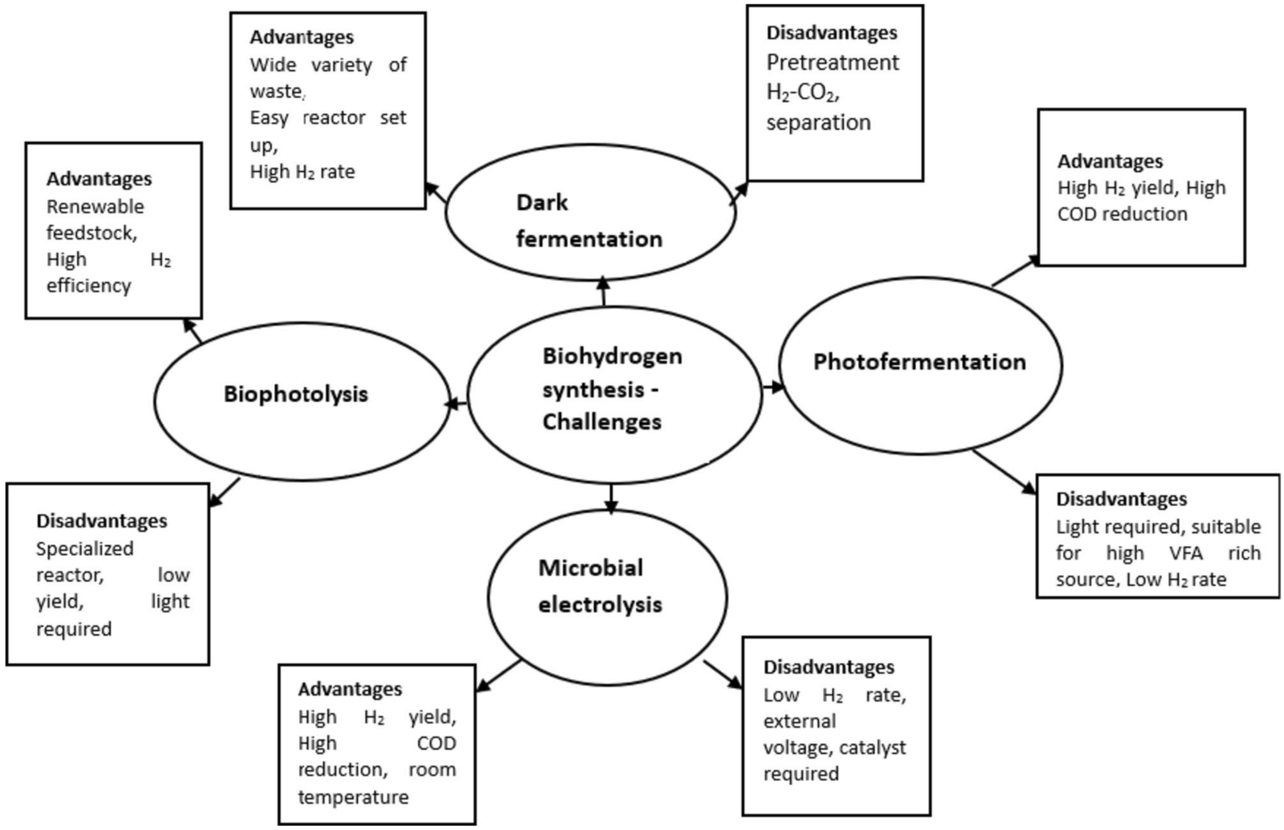

Fig. 10 Advantages and disadvantages of biohydrogen synthesis Methods

low hydrogen rate. Also, it needs catalyst for electrode and external electricity [33]. There is need to explore various microorganisms and feedstocks to overcome the disadvantages of the hydrogen production methods. Combinations or integration of different technics can overcome the disadvantages of these technics. Figure 10 depicts the advantages and challenges (disadvantages) faced in biohydrogen synthesis by various methods.

7 Conclusion

Hydrogen is considered as the fuel of next generation that can be used for industrial and vehicle fuel requirements. Storage of hydrogen is tricky issue due to its low volumetric energy density. Aspects of biohydrogen synthesis like the feed stocks, microorganisms, equipment, and yield are widely reported in various articles. As various innovative approaches and methodologies or combinations of the same are being explored by the investigators, there are needs to keep the research community updated. The approaches for bio hydrogen synthesis from waste include (a) water splitting by synthetic algae, (b) dark fermentation, and (c) photo fermentation. Studies indicate that prevention of hydrogen loss through acetogenesis on fermentation is the thrust area in the hydrogen synthesis. Manipulating the temperature, agitation, and pH conditions is one way of reducing oxygen loss through acetogenesis. Recent investigations indicate that enzyme stability and hydrolytic efficiency can be increased by using genetic engineering, electric biohydrogenation, and nanomaterials. Recent investigations include pre-treatment of biomass for better yield, fermentation conditions, equipment, and substrate resource in biohydrogen synthesis. Modern approach includes application of artificial intelligence for data driven models that allows quick response approximation for fermentative biohydrogen production. Enzyme stability and hydrolytic efficiency can be increased by using genetic engineering, electric biohydrogenation, and nanomaterials.

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Declarations

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