Advanced biohydrogen production using pretreated industrial waste: Outlook and prospects

Desika Prabakar [a], Varshini T. Manimudi [a], Subha Suvetha K [b], Swetha Sampath [a], Durga Madhab Mahapatra [c], Karthik Rajendran [c], Arivalagan Pugazhendhi [d,*]

[a] Centre for Biotechnology, Anna University, Guindy, Chennai 600025

[b] Amity Institute of Biotechnology, Amity University, Noida, Uttar Pradesh 201303

[c] Department of Biological and Ecological Engineering, Oregon State University, Corvallis, Oregon 97331-3906, United States

[d*] Innovative Green Product Synthesis and Renewable Environment Development Research Group, Faculty of Environment and Labour Safety, Ton Duc Thang University, Ho Chi Minh City, Vietnam

***Corresponding Author Address:**

Dr. Arivalagan Pugazhendhi

Innovative Green Product Synthesis and Renewable Environment Development Research Group

Faculty of Environment and Labour Safety

Ton Duc Thang University

Ho Chi Minh City, Vietnam.

Email: arivalagan.pugazhendhi@tdt.edu.vn

Abstract

In order to address existing environmental concerns as a result of non-renewable energy sources and to meet future energy demands, biohydrogen offers a suitable alternative energy reserve. Discrete as well as integrative methods of biohydrogen production have been analyzed over time, optimized for achieving high yields. In addition, key process parameters such as temperature, pH, hydraulic retention time, substrate concentration etc., which influence the rate of production have been clarified. Several studies have exploited industrial waste as feed sources for the production of biohydrogen; however, lower yields from these add an additional requirement for suitable pretreatment methods. The present communication examines various pretreatment methods used to increase the accessibility of industrial wastewater/waste for biohydrogen production. Furthermore, a brief overview addresses challenges and constraints in creating a biohydrogen economy. The impacts of pretreating wastes on biohydrogen generation and the latest trends are also supplied. This study helps in the critical understanding of agro-industrial wastes for biohydrogen production, thereby encouraging future outcomes for a sustainable biohydrogen economy.

Keywords: Biohydrogen; non-renewable; pretreatment; wastewater; industrial waste.

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1. Introduction

Increasing awareness of environmental impacts of energy production and use has been growing steadily as a result of harmful effects which impact biota and biodiversity, and climate impacts specifically have brought environmental considerations to the fore. Petroleum-derived fossil energy sources are one of the major contributors of such complications. Prevailing issues regarding sustainability due to conventional practices has forced attention towards alternative energy sources including bio-based sources [1]. In this context, biohydrogen stands as an ideal alternative, offering an array of desirable attributes for efficient energy generation. Despite promising research activity, biohydrogen production processes still demand refinement on a broad scale owing to certain inhomogeneities, especially with respect to suitable reactor design and configuration. To devise an efficient method for the production of biohydrogen without compromising economic viability, research also focuses on employing waste matter (i.e. from industry) as a potentially favored substrate [2].

Biohydrogen production is known to be either a light-dependent (photofermentation) or a light-independent (dark fermentation) process (Fig. 1) [3]. Biohydrogen can be produced through different processes, namely: anoxic photosynthesis, fermentation, oxygenic photosynthesis, and cyanobacterial hydrogen biosynthesis through a nitrogenase enzyme complex. The integrative prospects offered by dark fermentation methods are well established despite being less commonly used by industry [4].

It is essential to optimize the key parameters which influence the production process. Studies have analyzed the effects of crucial parameters such as temperature, pH and substrate concentration on biohydrogen generation. For instance, Thanwised et al. [5] showed an inverse relationship between hydrogen production rate (HPR) and hydraulic retention time (HRT) and reported an optimum HRT of 6 h for anaerobic baffled reactor operation. Another variant, an "anaerobic sequencing batch biofilm reactor" has been tested for its effectiveness in biohydrogen production with varying organic loads and feed types [6]. Gomes et al. [7] established the unfavorable effects of lactic acid bacteria hindering hydrogen production using continuous multiple tube reactors. Hernández et al. [8] showed anaerobic co-digestion of substrates as an essential strategy for enhanced biohydrogen production with varying organic loads. Experiments reveal the importance of optimizing the carbon to nitrogen (C/N) ratio in order to attain desirable yields. Amidst such influencing factors, substrates hold a top priority owing to their role as energy source for adequate functioning of microbial metabolisms. In this context, cost-effective substrates are generally preferred, with special regard to industrial waste and wastewater.

Among studies utilizing agro-industrial waste for biohydrogen production, Venkata Mohan et al. [9] reported a hydrogen production of 6.076 mmol H_2/m^3/min using the composite chemical wastewater as a substrate, highlighting the benefits of simultaneous hydrogen production and wastewater treatment. High strength brewery industrial wastewater [10] showed a hydrogen yield of 259.6 mL H_2/g COD at a concentration of 5 g/L. Recently, mushroom farm waste has shown a peak hydrogen production rate of 6.84 mmol H_2/L/d at pH 8 and a substrate concentration of 60 g MW/L under batch fermentation conditions [11]. Strategies for simultaneous use of two different categories of wastewater as a nutrient source have also been explored. A combination of brewery wastewater (BW) and paper and pulp mill effluent (PPME) yielded 0.69 mol H_2/L medium at 10% BW + 90% PPME [12]. Nevertheless, biohydrogen yield obtained from the direct consumption of industrial waste is low unless incorporating an additional pretreatment.

Numerous studies have been conducted on the feasibility and effects of implementing pretreatment strategies to improve biohydrogen yield. He et al. [13] tested the solubilizing capacity of hydrothermal pretreatment (HTT) using rice straw for anaerobic production of biohydrogen. A maximum soluble substrate of 80 mg/g of volatile solids (VS) (210 ˚C and 0 min holding time) resulted in a 28 mL/gVS yield of biohydrogen, i.e., 93-fold higher than the control. In a recent study, real textile desizing wastewater was pretreated using a fused coagulant, GGEFloc-653 (montmorillonite, polyacrylamide and activated carbon) to achieve increased hydrogen yields [14]. Results illustrated an increase in the hydrogen production capability by 120% ((11-5 mL)/5 mL) with a yield of 3.9 L H_2/L/d, highlighting the potential of coagulation pretreatment generally. Further, combined pretreatment approaches such as chemical pretreatment followed by microbial electrolysis are well established [15]. For example, the highest hydrogen yield (8.5 mg H_2/g VSS with the energy efficiency of 138±8%) was obtained in one experiment using an SDS pretreatment comparing SDS, NaOH, per-acetic-acid and β-cyclodextrin pretreatments to concentrate volatile fatty acids (VFAs). The SDS resulted in a build-up of acetate and propionate, thereby intensifying biohydrogen production. An extensive overview of the effectiveness of assimilative pretreatment procedures for organic wastes is given by Ruggeri and Tommasi, [16] and provides valuable information for the implementation of pretreatment technologies.

The aim of the present communication is to provide an overall view of the various methods of biohydrogen production using pretreated agro-industrial wastes. The strategies and approaches explored until now along with their positive and negative features are discussed. Moreover, key parameters influencing biohydrogen production and the importance of their standardization are highlighted. Various pretreatment techniques facilitating anaerobic digestion for enhanced biohydrogen production and their effects on yield and production rate are also described. Reaction mechanisms present during waste pretreatment and their beneficial roles have been analyzed and presented systematically. Moreover, a schematic representation of the flow process occurring during biohydrogen production is proposed that emphasizes the biorefinery approach, to aid the development of biohydrogen-based economy with infusion of industrial waste and discharge.

2. Biohydrogen production from industrial and toxic wastewater

Biohydrogen production is a well-established process that can utilize several methods, of which the most fundamental is waste-splitting photosynthesis or biophotolysis. In this process, just water and sunlight suffices the oxygenic photosynthetic microorganisms such as green algae and cyanobacteria for effective biohydrogen generation. Two different approaches of biophotolysis exist, namely, the direct process, which involves an instantaneous conversion of the readily available substrate; and the indirect process, in which CO_2 is first taken up and subsequently utilized in the biohydrogen production [17]. Conversely, the widely-investigated dark fermentation utilizes anaerobic metabolism. Under anaerobic conditions, synthesized pyruvate enters into the acidogenic pathway forming VFAs as substrates for biohydrogen production. Despite its faster rate, the anaerobic pathway presents a disadvantage in its byproduct formation, resulting in biohydrogen inhibition [18]. In order to overcome this, integrated approaches have been adopted, among which the most common is successive dark and photofermentations. Moreover, effluents from dark fermentation can also be combined with microbial electrolysis cells, providing high efficiency and ease of process [19]. A schematic of various biohydrogen production processes is depicted in Fig. 2.

The aforementioned pathways are each significantly affected by critical factors that can increase or decrease hydrogen yield. Hence, understanding these factors aids in fine-tuning the entire production process.

2.1 Factors influencing the performance of biohydrogen production

Biohydrogen production from wastewater can provide various complementary benefits, i.e. waste minimization, waste utilization and simultaneous energy generation [20]. At present, only 1% of biomass is being used for hydrogen production. However, biohydrogen production processes are gaining importance mainly for two reasons: ease of operation at ambient conditions (temperature and pressure) and increased efficiency while utilizing renewable energy resources [21]. Hence, understanding the physical factors affecting biohydrogen production is vital.

2.1.1 Temperature

Buitrón et al. [22] examined the effects of temperature, initial substrate concentration, and hydraulic retention time (HRT) on biohydrogen generation from *Tequila vinasses* using an anaerobic sequencing batch reactor. The results showed significant production of biogas at 25 °C with 12 h HRT, while both biogas and hydrogen were produced at 35 °C and 24 h HRT. About 29.2±8.8% hydrogen was found in the biogas while the substrate concentration was 3 g COD/L at 35 °C with 12 h HRT. The authors concluded that out of all the parameters analysed, HRT had the greater impact on hydrogen yield, while temperature strengthened the process. In a similar experiment, Gadow et al. [23] showed that the thermophilic and hyperthermophilic conditions produced better results than mesophilic conditions. In addition, a recent research by Sotelo-Navarro et al. [24] assessed the viability of disposable diapers for the production of biohydrogen while evaluating the influences of temperature and substrate concentration. Batch reactors were loaded with the substrate containing 25% total solids, and 10% w/w inoculum. The results showed that the biohydrogen production at 55 °C was higher than at 35 °C, which could be attributed to the increased pace of microbial metabolism in the thermophilic regime.

2.1.2 pH

Biohydrogen production during dark fermentation processes is inhibited at low culture pH (<4.0). Li et al. [34] examined the influence of pH on hydrogen production from liquid swine manure supplemented with glucose in an anaerobic sequencing batch reactor. The results showed a rapid increase in hydrogen content from 0.14% at pH 5.6 to 33.57% at pH 5. Nonetheless, the hydrogen content declined to 13.66% at pH 4.7. It was shown that pH values below 5 incurred instabilities to the reactor, thereby, bringing about an unfavorable environment and the lower outcome. Ghimire et al. [35] investigated the influence of culture pH and hydrogen production stability during the dark fermentation of cheese whey (which is rich in carbohydrate but provides acidic pH), supplemented with buffalo manure (characterized by high alkaline pH). The outcome of the investigation showed that at the ratio of 4 gVS/gVS (cheese whey to buffalo manure) and an organic loading rate of 2.1 gVS/L/d cheese whey at a stable culture pH of 4.8-5.0 the maximum hydrogen yield and the production rate were 152.2 (±43.9) mL H_2/gVS and 215.4 (±62.1) mL H_2/L/d, respectively. The use of buffalo manure improved the hydrogen production stability and could potentially replace chemical buffering agents used in large scale dark fermentation applications. Likewise, Xiao et al. [36] studied the impacts of varying the pH of protein wastewater used as a feedstock for biohydrogen production. The results showed that pH 12 pre-treatment brought about a major decline in the α-helix content of protein from 69.1% to

42.4% yet no hydrogen was produced. However, when fermented, pH varied between 7 and 10; and the anaerobic metabolic reaction of amino acids shifted from propionic acid to acetic acid, which enhanced the activity of key enzymes, resulting in a maximal hydrogen production of 205.2 mL/g-protein.

2.1.3 Dilution rate

Han and Shin, [37] examined the effects of dilution rate (D) on hydrogen fermentation of food waste (FW) pretreated by heat shock. It was found that the fermentation efficiency (58%) at an initial D of 4.5/d was higher than the efficiencies obtained (51.4, 55.2, and 53.7%) at initial D of 2.1, 3.6, and 5.5/d, respectively. Further, the fermentation efficiency had surged up to 70.8% when the dilution rate was changed from 4.5/d to 2.3/d. This improved efficiency was credited to the extreme deterioration of slowly degrading material based on the effective conversion of COD to hydrogen (19.3%), VFA (36.5%), and ethanol (15.0%). Radjaram and Saravanane [38] reported that at a constant HRT of 30 h, a maximum biohydrogen production of 7960 mL/d was observed at an optimized dilution ratio of 1:10 (press mud to sewage). A study by Hwang et al. [39] reported the importance of standardizing the dilution ratio with respect to photoheterotrophic microalgal biomass for biohydrogen production. The results showed a complex pattern as the increase in dilution ratio decreased the hydrogen production at pH 6.8, 8.0 and 9.0, respectively though such a situation was not witnessed at pH 4.9. Moreover, the maximum hydrogen production (191.2±14.7 mL/L) was obtained at pH 8.0 only when the undiluted effluent was utilized as higher dilution ratios significantly hindered the effective digestion by microbes.

2.1.4 C/N ratio

Several studies highlight the importance of standardizing the C/N ratio; extreme ratios can create considerable negative effects on biohydrogen production. Rughoonundun et al. [40] showed that optimum C/N ratios would facilitate microbial metabolisms. An optimum range of C/N ratios between 13 and 25 was reported for the co-digestion of wastewater sludge and pretreated bagasse as nitrogen deficiency was found to hinder microbial growth beyond that range (for instance, 30 g C/g N). Likewise, Anzola-Rojas et al. [41] proposed that a moderate-to-very-high nitrogen concentration (C/N < 137) would contribute to excessive cell growth while trace levels of nitrogen (C/N > 137) would inhibit enzymatic activity. It was also found that C/N ratio had no effect on fermentation patterns. Similarly, Farghaly et al. [42] examined biohydrogen production using a multiphase anaerobic reactor with paperboard mill wastewater as the nutrient source wherein the highest hydrogen production rate (HPR) was obtained at a C/N ratio of 47.9. These observations illustrate the importance of optimizing C/N ratio in enhancing microbial metabolisms for hydrogen production.

2.1.5 Substrate concentration

Synthetic wastewater solution was used as a substrate for biological hydrogen production using *Clostridium beijerinckii* [43]. The results showed positive effects on hydrogen production rates upon increased pH (5.7–6.5) and substrate loading (1–3 g COD/L). The optimal pH and substrate loading (6.3 and 2.5 g COD/L, respectively) yielded a maximal production rate of 71 mL H_2/L/h. Likewise, experiments on sweet sorghum extract showed high hydrogen productivity with an increase in carbohydrate concentration (9.89 to 17.5 g/L). The study also revealed that a switchover from C fixation to alcohols through bacterial metabolism decreased overall hydrogen production [44]. Likewise, Sreela-or et al. [29] studied the effect of inoculum concentration, substrate concentration and citrate buffer concentration on hydrogen yield from food waste. The maximum hydrogen yield and a specific hydrogen production rate (SHPR) of 104.79 mL H_2/gVS$_{added}$ and 16.90 mL H_2/gVSS.h, respectively were obtained at 2.30 gVSS/L of inoculum, 2.54 gVS/L of substrate, and 0.11 M of citrate buffer. Hence, substrate and citrate buffer concentrations had the greatest impact on specific hydrogen production rate (P = 0.0075); however, their effects on hydrogen yield (P = 0.0131) were even more intense. Further, Argun and Kargi [45] reviewed that batch operations witnessed inhibitory effects because of high initial substrate and final product concentrations, while the continuous mode of operation was mainly impacted by HRT. The fed-batch operation was deduced to be an effective method to overcome both substrate and product inhibitions compared with the continuous mode.

2.1.6 Organic loading rate

Djalma Nunes Ferraz Júnior et al. [46] investigated the effects of organic loading rate (OLR) on hydrogen production when sugarcane bagasse was continuously fed in an upflow anaerobic packed bed reactor. The hydrogen production and yield were found to rise with OLR increasing between 36.2 kgCOD/ m^3/d and 72.4 kgCOD/ m^3/d. Such an outcome was attributed to the increased copies of Fe-hydrogenase genes, which brought down the negative interference of oxygen in the system and enabled continuous hydrogen production. Additionally, Lin et al. [47] also reviewed various factors influencing biohydrogen production and established a suitable range of key parameters such as substrate concentration of 0.25-160 gCOD/L, pH (4-8), temperature (23-60 °C) and HRT between 0.5-72 h with various types of reactor configurations to yield significant amounts of biohydrogen. The highest hydrogen production was observed at an organic loading rate (OLR) of 320 gCOD/L/d, a substrate concentration of 40 gCOD/L, HRT of 3 h, a pH between 5.5-6.0 and a temperature of 35 °C in a continuously-stirred tank reactor system using mixed cultures, fed with condensed molasses-fermented soluble wastewater.

2.1.7 Hydraulic retention time

Badiei et al. [48] recognized the critical role of HRT in hydrogen production and showed that during unfavorable conditions, non-hydrogen producing bacteria would increase causing lower yields beyond the optimum HRT of 72 h for diluted palm oil mill effluent (POME) in an anaerobic sequencing batch reactor (ASBR) system. A reduction in HRT caused the washing out of active bacteria from the system subsequently hindering hydrogen production. Likewise, Scoma et al. [49] assessed the influence of HRT on the anaerobic acidogenic process with dephenolized olive mill wastewater (OMW). Reduced HRTs contributed to higher hydrogen production rates. With a 7-fold decrease in the HRT (7 to 1 day), a 30-fold increase in hydrogen was recorded. Co-fermentation studies yielding both hydrogen and methane also showed major dependencies on HRT that significantly contributed to the standardization of the desired product. Rosa et al. [50] showed that no appearance of methane and a hydrogen yield of 0.7 mmol H_2/g COD(AFBR1) and 1.0 mmol H_2/g COD (AFBR2) were achieved, respectively at an HRT of 10 h.

2.1.8 Critical factors

Certain critical factors such as inoculum age and volume as well as the concentration of H_2SO_4 contribute to enhanced biohydrogen production. Optimizing inoculum age improved the rate of hydrogen production as well as total biohydrogen generated. Experimental results indicated a drop in biohydrogen production when an inoculum of high culture age was used [51] and an early stationary phase of the culture would be appropriate for increased hydrogen production [52]. However, in certain cases, the inoculum from the exponential phase (36–48 h of culture incubation) was more desirable [53, 54]. Kotay and Das [55] studied hydrogen production using *Bacillus* strain isolated from anaerobic sludge and inoculum with ages from 10–18 h were used. When a 14 h old inoculum was used, there was a decline in the lag-phase, subsequently increasing hydrogen production. Similarly, *Rhodopseudomonas* sp. with an inoculum age of 14 h (mid-exponential culture) produced the maximum hydrogen yield of 160 mL H_2/60 mL-vessel via photo fermentation [56].

Even more than age of the inoculum, size of the inoculum was shown to hold a greater importance. Prakasham et al. [57] carried out statistical analysis using ANOVA, which revealed that inoculum size was the most influential factor for biohydrogen production (39%) among nutrient ratio, medium pH, inoculum size and age. Furthermore, various studies have shown that aerobic and anaerobic cultures have expressed varied behaviours on account of changing the volume of the inoculum. About 10% v/v inoculum size produced the maximum hydrogen yield of 23.95 mL for an anaerobic culture whereas 5% v/v exhibited the highest yield for aerobic cultures (21.8 mL) [58]. In another case, when 12.5% volume of the inoculum isolated from cow dung was utilized for hydrogen production, the maximum biohydrogen production rate of 355.2 mL/L/h was attained. Both inoculum size and volume caused production increase with an increasing range yet began to decline after a certain point [59]. This could be due to a higher amount of carbon being supplied towards biomass formation in lieu of biohydrogen generation [60].

Some other studies have analyzed other components which have been found to influence biohydrogen production. For instance, Eroglu et al. [61] studied the effects of iron and molybdenum addition on biohydrogen production from olive mill wastewater. It was found that Mo slightly enriched the total volume of hydrogen gas production (62 mL H_2) in comparison with a control reactor (40 mL H_2). However, a significant rise in hydrogen production (125 mL H_2) was observed when Fe-supplemented cultures were utilized, highlighting the potential importance of metal ions for enhanced biohydrogen generation. Wang et al. [62] studied the influence of polyhydroxyalkanoates (PHA) in waste-activated sludge on hydrogen yield. It was observed that with the increase in the sludge PHA (25 to 178 mg/g VSS), the hydrogen production also increased from 26.5 to 58.7 mL/g VSS owing to effective solubilization. In contrast, when sludge containing polyhydroxyvalerate (PHV) was utilized, a drop from 51.2 to 41.1 mL/g VSS was recorded. Sharma et al. [63] studied the effects of utilizing a mixture of several wastes. It was reported that slaughterhouse liquid waste (SL), brewery waste biomass (BWB) and urea each amplified biohydrogen production by 18.81±3.56, 27.30±3.54 and 38.57±3.66%, respectively. Hence, there exist an array of parameters which can or need to be explored, subject to each particular waste/s substrate being analyzed. It is essential to understand crucial supplementation that can positively influence biohydrogen production, especially during pilot-scale reactor experiments. Figure 3 shows various factors that influence biohydrogen production. Various crucial parameters influencing hydrogen production have likewise been listed in Table 1.

2.2 Feedstock quality

As a sustainable feedstock, biomass is the source for hydrogen production using dark fermentation technology. Feedstocks for favorable hydrogen production include agricultural crops, lignocelluloses, food waste, aquatic plants and algae and municipal effluents. Optimization pressure is high, and noteworthy research has even been carried out on hydrogen production from engineered algae [64]. Crucial criteria in the selection of feedstock are substrate availability, cost, carbohydrate content and biodegradability [65]. Based on the nature and type of feedstock, biofuel can be classed into first, second and third generations, respectively. First generation biofuels are produced from food commodities whereas second-generation biofuels are generated by lignocellulosic biomass, such as wood chips, energy crops, agricultural and forest residues and cheap municipal and industrial wastes. While, algae are the most promising leading edge the third generation biofuels [64, 66].

2.2.1 First generation feedstock

Hydrogen generation is a growth-associated process, with increased microbial growth contributing to higher hydrogen production. Optimizing production is a major concern of various primary-feedstock studies. Azman et al. [67] investigated hydrogen production from de-oiled rice bran using *Clostridium acetobutylicum* YM1. The study revealed no relationship between initial pH and the incubation temperature, and the volume of the inoculum. However, an increase in inoculum volume contributed to increased hydrogen yields while higher inoculum volumes insignificantly affected hydrogen production. In this context, Guerrero et al. [68] proposed optimal reaction conditions for the production of hydrogen through the slow pyrolysis of apple pomace. The study showed a maximum hydrogen production at 715 °C along with a dry-base composition of 73.0% H_2, 19.1% CO, 5.3% CO_2 and 2.5% CH_4 with no carbon formation.

Food waste is a primary contributor of clean fuel production. The increasing global food crisis and future food security pose a major threat to the viability of first-generation biofuel production. Hence, biohydrogen production from co-products (lactose, lactic acid and proteins) derived from whey are alternative, favorable bioprocesses that are techno-economically feasible with minimal environmental issues. Whey is considered a suitable feedstock for hydrogen production (even more than sugar minimal media) owing to its rich carbohydrate content present together with organic acids. For example, a maximum biohydrogen yield of 6.35±0.2 mol H_2/mol-lactose was obtained with whey in one set of experiments, while an in-house isolate of *Clostridium* sp. IODB-O3 inoculated in a sterilized medium unveiled a best hydrogen yield of 5.9 ± 0.3 mol H_2/mol lactose [69].

2.2.2 Second generation feedstock

Lignocellulosic biomass is a popular source on account of its abundant availability [64]. A diverse range of compost including green compost (ACV) that are made from tree and yard wastes, crop residues and other wastes of plant origin; brown compost (ACM) obtained from municipal organic waste, kitchen and canteen waste, animal manure have been studied for hydrogen production. Arizzi et al. [70] utilized three types of green compost (ACV1, ACV2 and ACV3), immature compost in bio-oxidation phase (ACV15) and a raw mixture of composting process (“Mix”) for biohydrogen production and reported a hydrogen production rate of 0.02–2.45 mL H_2/g VS.

Sewage sludge (SS) is also a sustainable source for fermentative hydrogen production. Sludge from municipal waste plays an important role as a rich source of carbohydrates and glycerol for hydrogen production. The main limitation of sludge utilization is its low carbon to nitrogen ratio, thus, its lower yield production. Here, the pretreatment of sludge has been proven to enhance hydrogen production. Among pretreatments, physical methods are the most studied, and these include heat, ultrasound, microwave and UV-light, plus sterilization protocols. However, a diverse range of studies indicate that integrated pretreatment methods such as heat-alkali, heat-ozone, heat-ultrasound, heat-acid, alkali-ionizing radiation, sterilization-enzyme, ultrasound-alkali, and heat-ozone-ultrasound pretreatments are more effective than individual pretreatments [71].

2.2.3 Third generation feedstock

Algae are advantageous for biohydrogen production in conjunction with biodiesel generation [72, 73] as they have shorter doubling times (2–5 days) relative to other feedstock sources [64]. On this front, Batista et al. [74] produced hydrogen from a microalgal biomass of *Scenedesmus obliquus* using *Enterobacter aerogenes* and *Clostridium butyricum*. It was observed that 2.5 g_{alga}/L *Enterobacter aerogenes* produced 57.6 mL H_2/g VS_{alga} of hydrogen whereas 50 g_{alga}/L *Clostridium butyricum* produced 113.1 mL H_2/g VS_{alga}. It was also noted that wet algae production outcomes were similar to dry, and sometimes biohydrogen with high purity. Likewise, utilization of wet algae removed the drying step, thus leading to energy and time savings. However, production of hydrogen from algae via dark fermentative technology is limited by carbohydrate hydrolysis.

In order to achieve high carbohydrate hydrolysis for an increased hydrogen production, algae are to be pretreated. The most widely used pretreatments are physical (milling, ultrasonic, microwave), thermal (LHW, steam explosion,) and thermochemical (diluted acid) pretreatments. However, utilization of thermal or thermochemical pretreatments contribute to the production of furfural, 5-HMF as a by-product that inhibits the activity of the hydrogen producing bacteria [75]. Further studies are required to study the impact of byproducts (furfural, 5-HMF).

In addition to algae, the aquatic invasive species *Eichhornia crassipes*, commonly known as water hyacinth has also been utilized to produce hydrogen via dark fermentative technology. Experiments revealed that an increase in water hyacinth (carbohydrate source) concentration decreased hydrogen production and after a point of time, the metabolic pathway switched to methane production due to low C/N ratios. Similarly, Lay et al. [76] achieved their highest hydrogen production rate of 1.1 mL/L/d at pH 4 with a retention time of 2 days. Pretreatment of water hyacinth with NaOH worked to improve hydrogen production rate up to 51.7 mL H_2/g total volatile solids [77].

3. Diverse industrial wastewater/waste explored for biohydrogen production

With growing concern over industrial effluents degrading the environment and affecting ecosystems, the conversion of such wastes into functional resources is being extensively studied, and several promising results have been obtained. A few of the various wastes that have been analyzed include cattle wastewater [78], paper and pulp mill effluents [79], effluents from citrus processing [80], chemical wastewater [9], waste activated sludge [81], beverage wastewater [82], coffee drink wastewater [31], cheese whey wastewater [83], distillery wastewater [84] and pharmaceutical wastewater [85]. Furthermore, the growth in biodiesel sector has led to enormous discharge of crude glycerol, which is also utilized as a substrate for biohydrogen production [73, 86, 87].

Moreover, since carbohydrate-rich industrial effluents are biodegradable, numerous studies have been done to understand their hydrogen production capabilities after pretreatment.

For instance, Shi et al. [88] reported a rise in the cumulative hydrogen yield of 127.26 mL/gTVS for sweet sorghum stalk pretreated with 0.4% NaOH compared to raw stalk (52.1 mL/gTVS). Similarly, El-Bery et al. [89] examined an alkali hydrolyzed rice straw feedstock for improved hydrogen production. Tosti et al. [90] showed the production of 3.25 kg of hydrogen per ton of Olive mill wastewater (OMW) using a noble-metal-based catalyst supported on rare earth mixed oxides that had been added to the OMW.

In addition, waste activated sludge has been analysed for its biohydrogen production potential, owing to its high polysaccharide and protein content [91]. Waste activated sludge (WAS) from fructose-processing as a substrate, resulted in 7.8 mmol H_2 at 55 ˚C and pH 7 [92]. A combined pretreatment of heat with an alkaline gas was applied to the sewage sludge, resulting in 85% solubilization, thereby facilitating biohydrogen production [93]. An augmentation of hydrogen production from WAS by microbial electrolysis cells was carried out by Lu et al. [94], wherein a higher hydrogen yield of 15.08±1.41 mgH_2/gVSS was attained compared to 5.67±0.61 mgH_2/gVSS using raw sludge. Liu et al. [95] analyzed different approaches for the pretreatment WAS wherein a photocatalytic pretreatment achieved a cumulative hydrogen yield of 211.0 mL/L-sludge, which was higher than those from UV pretreated WAS (111.0 mL/L-sludge) and raw WAS (93.0 mL/L-sludge), respectively. Continuous hydrogen production via co-digestion of the organic fraction of municipal solid waste and kitchen wastewater has also been reported [96].

Industrial waste in various forms have been investigated in order to obtain an understanding of their potential for biohydrogen production. For instance, a co-fermentation of water hyacinth (WH) and beverage wastewater in the form of powders and pellets in different ratios was investigated [97]. The pellet form was found to facilitate the higher hydrogen production of 13.65 mL/g feedstock using 1.6 g WH and 2.4 g BW. For hydrogen-producing organisms, industrial wastes are sometimes supplemented with other feedstocks and nutrient sources. For example, when sugar refinery wastewater was used as feed, there was a relatively low chemical oxygen demand (COD), and thus a supplementary sugar (sucrose) was mixed with the wastewater in order to meet the high substrate concentration [98]. Likewise, a lower ratio of COD: nitrogen: phosphorous (100:0.7:2.3) was recorded for cassava wastewater used in hydrogen production. An insufficient nitrogen content was then enhanced by the addition of NH_4HCO_3 [99]. In addition, Intanoo et al. [99] used a combination of agro-industrial wastes and byproducts namely cheese, fruit juice, paper, sugar, fruit processing and spirits for biohydrogen generation via a two-step process of a) dark fermentation and b) microbial electrolysis. The combination of such wastes provided a high hydrogen yield of 1608.6±266.2 mL H_2/g $COD_{consumed}$ coupled with a maximum COD removal of 78.5±5.7%. Similarly, mixed fruit peels (MFPs) and paper mill sludge (PMS) as co-substrates (MFPs: 30% and PMS: 70%) for anaerobic hydrogen fermentation not only showed a corresponding 3 and 2.24-fold increase in hydrogen generation compared to the separate fermentation but also reduced inhibitory substances [100]. In addition, bio-electrochemical hydrogen production was ~ 4 L H_2/d when combinations of substrates namely, glucose, diluted raw glycerol and real urban wastewater were used [101].

Challenging industrial waste has also been studied, in addition to agricultural waste with its more readily biodegradable components. For instance: simulated EDTA wastewater was converted into hydrogen following a photooxidation reaction supported by synthesized photocatalysis (Pt/TiO_2-AC) [102]. In addition, terephthalic acid wastewater [103] was used as a sacrificial reagent and showed a rise in the rate of photocatalytic hydrogen production, up to 1.8 mmol/g/h owing to the richness of metal and metallic ions (Fe^{2+} and Fe) in the wastewater. Likewise, Cho and Hoffmann [104] assessed the probability of electrolytic hydrogen production during the course of electrochemical wastewater treatment using a multifunction semiconductor anode coupled with a stainless-steel cathode. Overall, the tendency towards more cellulosic materials improves the deployment of industrial wastewater. Hence, adopting pretreatment strategies can enhance the traits of industrial wastewater, which may not render an absolute potential in raw forms.

4. Role of pretreatment in enhancing biohydrogen production

The characteristics of industrial wastewater bearing organic compounds together with readily fermentable sugars may require certain modifications so that the wastewater can show desirable properties as a substrate for hydrogen production. Hence, pretreatment of industrial wastewater has gained a growing importance due to its ability to turn wastes into beneficial feedstock [92].

A comparative analysis of the following three pretreatment methods was carried out for olive mill wastewater by Eroğlu et al. [105] namely a) chemical oxidation with ozone and Fenton's reagent, b) photodegradation by UV radiation and c) adsorption with clay/zeolite. The most productive and economic method was the pretreatment using clay, which yielded the highest hydrogen production potential of 31.5 m^3/m^3. Despite exhibiting 90% colour removal, the other two approaches were found to be unsuitable for hydrogen fermentation. Hence, clay pretreated olive mill effluent was suggested as an appropriate choice for photofermentation of hydrogen. Similarly, Leaño and Babel, [106] reported on the three possible pretreatment methods for cassava wastewater to improve batch production of biohydrogen. With respect to ultrasonication, the results showed an increase in hydrogen production by 29.2%, which was attributed to an augmented sugar release due to cavitation by ultrasonic waves. When a combination of enzymes (OPTIMASH BG®) was used, the hydrogen volume recorded at pH 7 was 4.24 mol H_2/g COD, with a surge of 51.4%, attributed to an effective break down of non-starch carbohydrates, i.e. the structural materials of plant cells. However, α-amylase as a pretreatment choice created a tremendous increase of 53.5% in hydrogen production. This was due to the nature of the enzyme and its effective hydrolysis of 1, 4-alpha-glucosidic linkages in polysaccharides, yielding dextrins and oligo- and monosaccharides, which contribute to enhanced hydrogen production.

Thermal methods as a pretreatment strategy were investigated in the case of raw cheese whey from dairy industry wherein the whey was subjected to heat treatment at 105 ˚C for 5 min in order to remove the lactic acid bacteria [83]. Hydrothermal pretreatment of wheat straw was performed in a pilot plant (100 kg/h capacity) by a successive approach using three serial reactors [107]. Firstly, a soaking step at 80 ˚C and residence time around 6 min, followed by heat treatment at 180 ˚C for 15 min and finally, a stage of heating at 190 ˚C for 3 min. Such an approach was found to facilitate the production of bioethanol, biohydrogen and biomethane. The research was based on a biorefinery concept.

One of the most efficient methods for improving production from food and agricultural wastes involves an acid/alkali pretreatment. Fan et al. [108] reported a 136-fold increase in biohydrogen production with a cumulative yield of 68.1 mL H_2/gTVS while using HCl pretreated wheat straw waste as opposed to raw wheat straw. Similarly, pretreatment using 1% HCl was carried out for tofu residues, a byproduct of bean curd processing and production [109]. It was found that when the medium was supplemented with sewage sludge as a co-substrate, the hydrogen yield and production rate increased to 1.48 mol H_2/mol $hexose_{added}$ and 161 mL H_2/L/h, respectively from those of 1.25 mol H_2/mol $hexose_{added}$ and 50 mL H_2/L/h, respectively for the acid-treated tofu residue. The pretreatment also facilitated the suppression of indigenous lactic acid bacteria and propionic acid bacteria as evident from the distribution results that depicted the wide presence of acetate, butyrate, lactate, and propionate. Further, Chong et al. [110] documented a cumulative hydrogen production of 690 mL H_2/L as a result of effective hydrolysis of the amorphous xylan to xylose in oil palm empty fruit bunch (OPEFB) by a simple acid pretreatment (6% (w/v) H_2SO_4). Al-Shorgani et al. [111] studied the effects of pretreatment on anaerobic production of biohydrogen from major agricultural wastes including rice bran (RB), de-oiled RB (DRB), sago starch (SS), and palm oil mill effluent (POME) using *Clostridium saccharoperbutylacetonicum*. The highest yield of 7627 mL H_2/L was obtained for acid pretreated DRB (treated with 1% H_2SO_4) and it was also found that a nearly equal yield (7020 mL H_2/L) was exhibited when the mixture of enzyme pretreated POME and SS was passed through a nonionic polymeric adsorbent resin. It was also noted that the presence of inhibitors, namely, furfural and 5-HMF along with Cl^- brought a decrease in the biohydrogen production. Tian et al. [112] proposed an enhancement to the alkali pretreated sugar cane bagasse (SCB), with the addition of $CaCO_3$ (20 mM), which increased the hydrogen production by 116.72% (97.83±5.19 mmol/L) over the control (~ 45 mmol/L). This was attributed to the exceptional degradability of the recalcitrant crystalline SCB together with the buffering capacity of carbonate because of alkali-$CaCO_3$ pretreatment.

A study by Saratale et al. [113] established another finding while using acid pretreated rice husk hydrolysate (RHH) for biohydrogen production. Raw RHH produced 2.93 mmol H_2/g reducing sugar. However, there was a drop in the hydrogen production while using the rice husks pretreated with 0.2 and 0.4 % acid hydrolysate (1.90 and 1.74 mmol H_2/g reducing sugar). This was believed to result from the presence of acidogenic metabolites (lactate, acetate, formate, and butyrate) present in the cellulosic hydrolysates, which were found to inhibit microbial growth as well as hydrogen production. The results obtained were in concordance with few other studies using acid-pretreated wastes for biohydrogen production [113-115]. Hence, the effect of pretreatment varies with the characteristics of the waste feedstock as well with its influence on the growth of the microorganisms for biohydrogen production.

Another method studied in order to enhance the hydrolysis of proteins in waste activated sludge is a pretreatment using TiO_2 photocatalysis, which works by altering the protein conformation, resulting in peptide hydrolysis [116]. In one set of experiments, the hydrogen yield obtained (11.7 mL H_2/g-VS) was observed to be 1.2-fold higher than the control, which was a direct result of the readily metabolized substrate. A novel bioelectrohydrolysis system (BEH) based on self-inducing electrogenic activity was fabricated [117] as a pretreatment strategy to amplify the biohydrogen production from food waste. An increased hydrogen production of 29.12 mL/h was attained, which was attributed to the alteration of polysaccharides to their relative monomers, thereby enabling effective hydrolysis. Another unique approach, combining steam explosion and alkaline delignification, was studied by Ratti et al. [118] as a pretreatment for sugarcane bagasse to aid the hydrolysis of cellulose to fermentable sugars. Pintucci et al. [119] carried out pretreatment using two different vegetable matrices (dry-Azolla and granular active carbon) for decolorization and reduction of polyphenols present in olive mill wastewater (OMW). Results showed a higher specific hydrogen photoevolution rate (13.5 mL/g(dw)/h) using OMW (diluted to 30% v: v) as opposed to a synthetic medium containing glucose and fructose (11.8 mL/g(dw)/h).

Recently, Cheng et al. [120] examined the ionic liquid N-methylmorpholine-N-oxide (NMMO) for the pretreatment of cassava residues in order to facilitate enzymatic hydrolysis and subsequent energy production. Analysis revealed an increase in hydrogen yield from 92.3 to 126 mL/g TVS. The strong polarity of the functional group N-O of NMMO contributed to the destruction of the hydrogen bonding network of the cassava residues, which in turn resulted in high accessibility of cellulose. Moreover, the drop in the crystallinity index of the cassava residues from 40 to 34 can attest to the enhanced solubility of the substrate, benefiting hydrogen production.

In another case, a two-stage system using methanogenesis as a pretreatment step was shown to be a suitable means for production of biohydrogen from the acidic cheese whey in a microbial electrolysis cell (MEC) [121]. Initially, when raw whey was used, there was an accumulation of volatile fatty acids, which brought about a drastic decline in pH from 7 to 3.8. Such an instantaneous shift to an acidic environment resulted in obstructing the exo-electrogenic microorganisms, thereby incurring a loss of electrochemical activity. However, in a two-stage process, the effluents from the first stage of energy production (using dark fermentation and MEC) were used in the second stage for complementary hydrogen production. Results showed that the complementary hydrogen production using the methanogenic reactor set-up provided a higher cathode hydrogen recovery (r_{cat}) of 63% when compared to that of 22%, which was attained using the effluent from the dark-fermentation H_2 production as a substrate.

Overall, it can be understood that the choice of the pretreatment method is exclusive to the properties of the wastewater being utilized as feed. Hence, thorough analysis of the characteristics of wastewater and components present coupled with information on inhibitory substances is mandatory for the selection of appropriate pretreatment facilitating biohydrogen production. Various pretreatment methods adopted for enhanced biohydrogen production are listed in Table 2.

5. Pretreatment of industrial waste to facilitate anaerobic digestion for enhanced biohydrogen production

Anaerobic digestion involves a series of biochemical reactions through which organic materials are converted into a mixture of methane and carbon dioxide by microorganisms in the absence of oxygen [141]. It is a classic method to reduce the volume and weight of sludge, remove harmful microbes and to enhance renewable energy production. Yet, the low rate of anaerobic digestion stands as a huge drawback; to overcome this, pretreatment methods have been developed over the years.

A wide array of sludge pre-conditioning technologies has been used to curtail the long residence time of anaerobic sludge digestion and consequently aid easier substrate consumption for biohydrogen production. For instance, exposing the sludge to high oxidative conditions (ozone) ruptured the cell walls resulting in the release of soluble COD, thus causing hydrolysis of the sludge [142, 143]. In another study, Hogan et al. [144] reported that using sonication as a pretreatment for waste activated sludge (WAS) resulted in a 3-fold increased assimilation in the anaerobic digestion process.

Kim et al. [145] studied the effects of anaerobic co-digestion on hydrogen production using food waste and heat-treated sewage sludge. There was a decrease in the yield of hydrogen when tests were conducted separately using FW and SS compared to a combination of both (122.9 mL/g carbohydrate-COD at the waste composition of 87:13 (FW: SS)). Such an increased yield was attributed to the enriched protein content and balanced carbon to nitrogen ultimately due to the addition of sewage sludge to food waste. Further, a high fermentation efficiency of 73.8% indicated that heat treating sludge was advantageous for increasing hydrogen production.

Likewise, Kim et al. [146] analyzed the hydrogen production from an anaerobic co-digestion of rice straw and sewage sludge. Heat-pretreated sludge with rice straw showed a decrease in hydrogen production compared with raw sludge. This observation was explained by a decrease in microbial diversity, thereby slowing the rice straw decomposition. However, by optimizing of the C/N ratio (25), a maximal hydrogen yield of 0.74 mmol H_2/g-VS straw was attained.

Zhou et al. [147] reported a significant increase in hydrogen production by 101% in batch anaerobic co-digestion using a FW + PS + WAS mixture (food waste (FW), primary sludge (PS), and waste activated sludge (WAS) - 80:15:5). Different pretreatment methods have also been adopted for sewage sludge namely thermal treatment, ultrasonication, alkalization, acidification and a combination of alkalization with ultrasonication for understanding their influences on biohydrogen production [148]. It was found that an integration of ultra-sonication and alkalization was the best approach yielding 13.8 mL H_2/g-$VSS_{consumed.}$ in one set of experiments, an observation ascribed to the destruction of the microbial cell wall and the collapse in flocs owing to effective pretreatment.

Guo et al. [149] carried out a bioelectrochemical pretreatment for hydrogen production in a single-chamber membrane-free microbial electrolysis cell (MEC) via the anaerobic digestion of sewage sludge. Ti/Ru electrodes were used for the study and an applied voltage of 1.4 improved hydrogen production by 1.7-5.2-fold. The increased hydrogen yield was caused by the presence of the electrodes, which brought about a thorough mixing of the sludge. Moreover, it was found that the supply of voltages in MECs escalated the transformation of soluble organics during the final stages of anaerobic digestion.

Recently, Rafieenia et al. [150] adopted an aerobic pretreatment of food waste (carbohydrate rich (C), protein rich (P) and lipid rich (L)) followed by a two-stage anaerobic digestion process for hydrogen production. After the first stage of AD, the aerobic pretreatment reduced the average hydrogen production for C (19%), L (24%), and P (33%) substrates. Kumar et al. [20] reported a higher hydrogen yield of 86 mL/g with reducing sugars added when acid pretreated de-oiled jatropha waste was employed for mesophilic hydrogen production. More research on scalability is essential to overcome both technical and economic challenges in the production, storage, and transportation of biohydrogen.

6. Types of pretreatment of industrial waste for biohydrogen production

6.1. Sonolysis pretreatment

Sonolysis, in simple terms, refers to the breakage of chemical bonds or the production of radicals using ultrasound waves. The mechanism of ultrasonication is based on acoustic cavitation from ultrasound waves of high power and low frequency (20–100 kHz). The cavitation enhances chemical reactions. An enormous amount of power density is provided within a short time, ultimately facilitating high-temperature and high-pressure chemical reactions [151].

Several studies have been conducted making use of ultrasonication as a pretreatment method with a view of enhancing biohydrogen production. For instance, dairy wastewater pretreated with five ultrasonic densities (from 0 to 0.2 W/mL) at five different intervals (from 6 to 14 min) evinced a synergistic effect on biodegradability and microbial expression. This, in turn, increased hydrogen production 2-fold in comparison with an unpretreated sample [152].

Budiman and Wu [153] examined the outcomes of using ultrasonic irradiation as a pretreatment for integrated effluents from palm oil and pulp and paper mills. A high solubilization of particulates, organics, tannin, lignin, cellulose and other complex organic compounds in the effluents was achieved during the mixing stage. Consequently, the ultrasonic pretreatment (70% amplitude; 45 min) increased the yield of hydrogen from 467 to 872.4 mL hydrogen. There was also a significant increase in the ratio of COD soluble/COD total (from 0.25 to 0.85) of the substrate available for consumption. However, the optimization of any pretreatment strategy for efficient biohydrogen production is bound to produce certain unfavourable factors as well. For instance, the presence of certain inhibitory compounds such as furans and phenolic compounds may be formed while using certain substrates [154]. In addition, although several laboratory-scale studies have revealed promising results, the jump to industrial-scale production of biohydrogen preceded by such pretreatment methods remains a difficult task [155].

6.2 Microwave pretreatment

Microwave pretreatment is the process of irradiation using electromagnetic waves of frequency 300 MHz-300 GHz, which in turn produces heat in polar liquids. This technique is known to cause disruption of the cell wall, thereby, increasing the solubility of the medium subjected to it. There is also a fair amount of heat generated during the process owing to the realignment of dipoles, which aids in disruption as well [156].

In a study Guo et al. [157], wastewater sludge was subjected to three different pretreatment methods, namely, sterilization, microwave irradiation and ultrasonication. The microwave-pretreated sludge provided a maximal hydrogen yield of 11.44 mL/g TCOD with a shorter lag time of 10 h. Further, it was noted that the microwave treated sludge resulted in a higher hydrogen yield compared to the ultrasonic treated sludge with a yield of only 4.68 mL/g TCOD. In a study conducted by Thungklin et al. [158], the organic matter contained in the sludge of poultry slaughter house wastewater (composed of carbohydrate, protein and fat) were liberated by pretreating the sludge with microwave radiation (850 W for 3 min). The pretreatment was found to inhibit the methanogenic bacteria that hinder hydrogen production. Experimental results showed a maximum hydrogen production of 132.10 mL H_2/L sludge and a marked decrease in soluble protein during the end of the fermentation process. Thus, it could be shown that the primary substrate feature for hydrogen production would be the protein from the poultry slaughter house sludge.

Despite the benefits of using microwave radiation for pretreating industrial waste, it is often necessary to use low intensity irradiation in order to avoid elevating the temperature of the system. This is because a high-temperature environment may lead to the formation of inhibitory compounds. Additionally, microwave pretreatment has a high energy requirement, which renders it uneconomical [155]. It is not commonly used in large-scale hydrogen production.

6.3 Acid/Alkali pretreatment

The acid/alkali pretreatment method is a widely adopted technique due to its rendering extremely high solubilization of substrates for easier digestion by microorganisms. Effective substrate consumption favours fermentation and directly contributes to the increased production of the desired products. For hemicellulose-containing substrates, an acid pretreatment is widely preferred [159] while for lignocellulosic substrates, an alkali pretreatment is usually adopted due to the effective break down of crystalline structures (i.e. crystalline cellulose) owing to saponification of ester bonds. The most commonly used acids are HCl and H_2SO_4 and NaOH is the most extensively used base for the pretreatment of wastewater [160].

In one set of experiments, sugar processing wastewater and beet-pulp were pretreated using different methods (alkaline, thermal, microwave, thermal-alkaline and microwave-alkaline pretreatments) to understand the suitability of these methods for enhanced hydrogen production [135]. Experimental analysis revealed that of all the approaches considered, the alkaline pretreated beet-pulp showed the highest hydrogen production of 115.6 mL H_2/g COD. Liu et al. [95] carried out a study on acid pretreated (55% H_2SO_4, 40 ˚C, 2 h) rice straw hydrolysate, which was found to show a lower yield of hydrogen of only 0.44 mol H_2/mol T-sugar in comparison to a higher yield of 1.89 mol H_2/mol T-sugar, previously obtained for a similar acid hydrolytic pretreatment of rice straw (3 wt% (acid/biomass), 150 ˚C, 1 h) [161]. The authors proposed that the decrease was likely due to hydrolysis occurring in the much stronger acidic environment, which resulted in the promotion of inhibitors, ultimately affecting hydrogen production.

Recently, Battista et al. [162] reported that a basic pretreatment with an addition of NaOH to OMW-OP mixture (Olive Mill Wastewater (OMW), Olive Pomace (OP)) resulted in a hydrogen yield of 1.98 NL/L with the highest percentage efficiency of ~20% compared with other pretreatment methods using ultrasonication and $CaCO_3$. This was attributed to the effective biological attack of NaOH on cellulose, resulting in the cracking of the structural links between the carbohydrates, which released glucose for utilization as a substrate. Though this type of pretreatment is economical and highly efficient, the corrosion of bioreactors caused upon prolonged contact is likely to raise complications during the fermentation process. Further, it is vital to optimize the concentration of acid/alkali precisely in order to obtain desired yields.

6.4 Thermal or heat-shock pretreatment

In order to maximize the solubilization of industrial waste, especially sludge (which is rich in organic nutrients), thermal pretreatment is carried out on a wide scale. Heat-shock is one of several pretreatment methods used for digested sludge. By boiling sludge for 20 min [163] during second batch cultivation, heat-shock treated sludge produced 2.65 mmol of hydrogen, which was lower than that of untreated sludge (3.8 mmol). This was explained by the possibility of heat causing the destruction of various non-spore-forming bacteria, causing a decrease in oxygen consumption, eventually decreasing the conversion of substrate into hydrogen. Kotay and Das [164] reported that thermal pretreatment resulted in better solubilization of proteins compared to using freeze-thawing or chemical supplementation. Utilizing pretreated sludge as the nutrient source, the hydrogen yield was enhanced by 1.5–4 times.

In another case, improved access to high cellulose content in bagasse residue was made by applying a thermal pretreatment (100 ˚C for 2 h), which loosened the fibre bundle, followed by hydrolysis by cellulase, favoring biohydrogen production [165]. A yield of 1.40 mmol/g total volatile solid was obtained. However, upon alkali treatment using NaOH (4 g/L), the yield increased to as high as 13.39 mmol/g total volatile solid. This increase was ascribed to a higher rate of delignification coupled with enhanced cellulase hydrolysis. More recently, Pagliaccia et al. [166] reported biohydrogen production using thermally pretreated substrates, namely, food waste (FW) and olive husks (OH). Results of the study showed an increase in hydrogen yield by more than 30% with respect to the untreated mixture (FW+OH), which was due to the presence of highly available solubilized material. The high conversion rate of 87 NL of H_2/kg VS fed was attained.

A thorough understanding of a system is essential to obtain high yields of desirable products via thermal pretreatment. With a comparative analysis, further optimization can be performed to obtain improved productivity. Likewise, long term studies have shown that repeated heat shock is necessary during fermentation to permanently inhibit certain hydrogen consumers. In such cases, pretreatment using a thermal method may not be a cost-effective approach [167, 168].

6.5 Biological and enzymatic pretreatment

Biological pretreatment works by increasing the rate of hydrolysis during fermentation as it breaks the cross-linked structures of lignocellulose-rich wastes. Cui et al. [169] established the strategy of enzymatic pretreatment for increasing hydrogen yields using poplar leaf waste. A maximum cumulative hydrogen yield of 44.92 mL/g-dry poplar leaves was acquired from enzyme-pretreated substrate (2% Vicozyme L: a mixture of arabanase, cellulase, b-glucanase, hemicellulase and xylanase), which was approximately 3-fold greater than from raw substrate and 1.34-fold greater than from acid pretreated substrate (4% HCl).

Massanet-Nicolau et al. [170] examined the potential of a novel enzymatic pretreatment approach to increase the solubilization of carbohydrates in primary sludge obtained from a sewage treatment plant. There was an increase in soluble carbohydrates from 2.6% to 13.5% of the total carbohydrates as a result of successful enzymatic pretreatment, which likely contributed to a hydrogen yield of 18.14 L H_2/kg dry solids at an optimum pH of 5.5. Cheng and Liu [171] developed a novel pretreatment method for enhancing hydrogen production using raw cornstalk mixed with fungal pretreated cornstalk (*Trichoderma reesei Rut* C-30). An increase in cellulase activity was observed, and this contributed to the high rate of hydrolysis of lignocellulosic components into soluble substances, thereby facilitating hydrogen fermentation. Moreover, a very high yield of 194.9 mL was obtained, which was about 209% greater than that obtained through the direct fermentation of raw cornstalk.

In another study, a comparative analysis between enzymatic and acid hydrolysis as a pretreatment method for rice mill wastewater was set up [133]. The enzyme hydrolysis using *Aspergillus niger* produced 1.74 mol H_2/mol reducing sugar, which was higher than via an acid hydrolysis pretreatment (1.40 mol H_2/mol reducing sugar). A more recent study by Contreras-Dávila et al. [172] used *Agave tequilana* bagasse pretreated by enzyme hydrolysis (Celluclast 1.5 L®) for long-term continuous hydrogen production in both a continuous stirred tank reactor (CSTR) and a trickling bed reactor (TBR). The TBR exhibited higher hydrogen production (1.53 mol H_2/mol substrate) than CSTR (1.35 mol H_2/mol substrate). Biological pretreatment methods are cost effective as the energy required is often less than other protocols. Despite this and other positive traits in using biological pretreatment methods, there are a few common difficulties as well. For example, the compatibility of the enzymes used with the particular microbial consortia needs to be assessed in order to avoid the possible inactivation of the enzymes, which can cause a negative impact on hydrogen production.

6.6. Integrated pretreatment

Over time, a preference towards integrated pretreatment methods has emerged, revealing very good outcomes. For instance, Ozkan et al. [135] studied a combination of thermal-alkaline and microwave-alkaline pretreatments of sugar beet pulp for dark fermentative hydrogen production. High solubilization ratios were observed in both methods, while the thermal-alkaline pretreated beet pulp exhibited a higher rate (43.6%) compared to the microwave-alkaline pretreated beet-pulp (36.9%). A maximum hydrogen production of 148.5 mL was obtained for the former while the latter attained a cumulative biohydrogen yield of 134.0 mL. Further, the experiments were able to establish an order of increased hydrogen production efficiencies, as UA

> ultrasonic > UH > heat > UB > acid > base (UA- ultra-sonication+acid; UH- ultra-sonication+heat; UB- ultra-sonication+base). This is typical of combined pretreatment methods for enhanced biohydrogen production. Elbeshbishy et al. [173], likewise, determined suitable pretreatment methods for food waste using both individual and integrated techniques. Results showed that ultra-sonication with acid pretreatment showed the highest hydrogen yield of 118 mL/g $VS_{initial}$.

In another case, a novel dynamic microwave-assisted alkali pretreatment (DMAP) protocol for cornstalk (CS) was developed for the effective removal of lignin, and to increase the accessibility of soluble compounds by microorganisms [116]. Under optimized conditions, after CS pretreatment by DMAP for 45 min with an alkali loading of 0.12 NaOH g^{-1}, a liquid/solid ratio 50:1 (mL:g) and flow rate of 60 mL s^{-1}, a hydrogen yield of 105.61 mL g^{-1} of CS was achieved. The yield obtained was found to be 54.8% higher than that of untreated CS. In general, a pilot analysis of diverse pretreatment combinations is a natural prerequisite to establish a largescale integrated assembly for biohydrogen production. Economic feasibility and reusability studies also need to be carried out in the context of hybrid pretreatment approaches for industrial wastewater/sludge. A schematic representation of the various pretreatment processes for achieving viable biohydrogen production is provided in Fig. 4.

7. Trending pretreatment technologies for improved biohydrogen production

Apart from traditional pretreatment methods, various other pretreatment techniques have recently been used for enhanced hydrogen production. In one such case, red mud, which is a solid waste from bauxite refining industries, was modified for utilization in hydrogen production [174]. The use of calcinated red mud at 10 g/L (CRM: a non-toxic version of red mud) as a pretreatment for brewers' spent grain yielded a high specific hydrogen production of 198.62 mL/g-VS. The increased hydrogen yield was credited to several factors, namely, the effective degradation of cellulose and hemicellulose (which was evident from FTIR spectral peaks). The weakening of linkage bonds between ester and holocellulose and the degradation of the complex structure of hemicellulose were also observed. Such results were further validated by an extreme decrease in the crystallinity index of brewers' spent grain (BSG) from 24.1% to 4.5% as the CRM concentration rose to 20 g/L.

Yin and Wang [175] reported the pretreatment of waste-activated sludge using a low-pressure wet oxidation method for biohydrogen production with a considerable capacity for carbon recovery. Quantitative analysis revealed substantial improvements in concentrations of protein and polysaccharides by 102.5 and 2.2 times, respectively, after low-pressure wet oxidation treatment. A volumetric hydrogen production rate of 13.4−24.6 mL/h/L was obtained using the pretreated sludge. This pretreatment method was effective in the disruption of the sludge floc structure, thus aiding the release of intracellular compounds for ingestion by microorganisms. Another interesting pretreatment technique was explored [176] using ethanol organosolv as a pretreatment for rice straw to increase hydrogen production. After pretreatment, two fractions were obtained, namely, solid fraction rich in cellulose, which was used as the feed, and a liquid effluent fraction comprising hemicellulose and monomers, plus inhibitors including furans and the extracted lignin. This effective degradation of unfavorable components yielded 19.73 mL H_2/g of straw at an ethanol concentration of 45% v/v (180 °C for 30 min).

Nanoparticles have entered the field of renewable energy production. An experiment conducted by Gadhe et al. [177] involved the addition of nickel oxide (NiO) and hematite (Fe_2O_3) nanoparticles (NPs) to batch fermentation of distillery wastewater, and a greater enhancement in hydrogen production than control was observed. The co-addition of Fe_2O_3 and NiO NP was found to increase the hydrogen yield by an order of 1.2-4.5 more than the output using individual NP addition. A maximum specific hydrogen production rate of about 18.14 mmol/gVSS.d was obtained at an optimized NP supplementation (Fe_2O_3 plus NiO NP at 200:5) with an exceptionally high rise of 221% when compared to the control. Gadhe et al. [152] described a plausible mechanism for improved hydrogen yields as a result of the surface effects provided by NPs. Such effects contributed to improved electron adsorption in the hydrogen production pathway, which in turn enhanced the rates of enzyme-catalyzed reactions. Moreover, at optimized NPs loading, the duo played the role of scaffold facilitating enzyme-substrate binding at juxtaposition, which consequently caused both surface and quantum size effects that intensified the hydrogenase activity. Hydrogen production was the direct result of the enhanced activity of the *ferredoxin oxidoreductase*, *ferredoxin* and *hydrogenase*, which are key enzymes in the hydrogen production pathway. Likewise, Taherdanak et al. [178] reported the influences of FeO and NiO NPs on starch-derived mesophilic dark hydrogen fermentation. A maximum hydrogen production of 147.3 mL/g-VS was observed at a starch concentration of 5 g/L, and FeO and NiO NPs concentrations of 37.5 mg/L.

Very recently, Reddy et al. [179] established the role of magnetic NPs in improving hydrogen yields on acid pretreated sugarcane bagasse hydrolysate. Incorporation of Fe^{2+} (200 mg/L) and magnetite NPs (200 mg/L) exhibited an increase in the hydrogen yields as high as 62.1% and 69.6%, respectively. Moreover, the outcome of electron-equivalent balance demonstrated the greater effect of the magnetite NPs, apparent from the highly directed electrons-to-protons fraction, reaching up to 9.8%. Elreedy et al. [180] analyzed the impacts of Ni NP and Ni-graphene nanocomposite (Ni-Gr NC) on hydrogen production from industrial wastewater containing mono-ethylene glycol (MEG). Ni-Gr NC showed a higher hydrogen yield of 41.28 ± 1.69 mL/g COD initial *i.e*. 105% increase in production compared to the control. This study highlighted the importance of NP on graphene due to its providing a uniform dispersion of the Ni. Additionally, the findings were attributed to the unique electronic properties of Ni-Gr NC, which contributed to the enhancement of the associated catalytic reactions during AD process, ultimately resulting in a surge in the hydrogen produced.

Despite the significant influences of NPs on the yield of hydrogen, it is of paramount importance to take the negative effects into account and perform studies to resolve them. One such issue is of observed oxidative stress, which causes an instability of enzymes in the production pathway. In addition, a question that needs to be asked for largescale hydrogen production using NPs is that of possible toxic outputs from such an industrial set-up. Hence, studies need to be carried out to optimize the use of NPs in an ecofriendly way that fosters both energy production and sustainability.

Supercritical CO_2 can also be used as a pretreatment method for industrial waste. Supercritical here refers to using carbon dioxide above its critical point of temperature and pressure wherein the carbon dioxide behaves as a hybrid state in between gas and liquid. The supercritical conditions for carbon dioxide are 31.10 °C and 1031 psi. However, typical CO_2 pretreatments employ a pressure greater than the above-mentioned conditions, preferably 3000 psi. Higher sugar yields up to 20% of the theoretical sugar release have been reported in the past while using supercritical carbon dioxide [181, 182]. Similar to steam explosion, supercritical carbon dioxide when introduced reacts with the industrial waste, impregnates the biomass, and allows the release of sugars that can be subsequently used for hydrogen production. Recycled paper, and pulp industrial waste have used carbon dioxide explosion for the release of sugars in the past [183].

8. Feasibility of biohydrogen production from industrial waste

Hydrogen combustion is environmental friendly as it produces high energy upon burning with only water as its byproduct [184]. Hydrogen production from waste is systematically commendable as it is a possible way to reduce pollution. Despite different methods available for hydrogen production, dark fermentation is the simplest one [185]. Han et al. [186] produced biohydrogen from hydrolyzed food waste. The glucose was eliminated from the food waste by hydrolysis using commercial glucoamylase. Hydrogen yields of 245.7 mL H_2/g glucose (1.97 mol H_2/mol glucose) and 8.02 mmol/ (h·L) were obtained in batch and continuous systems, respectively. Furthermore, the hydrogen yield from industrial waste through a two-step process was 41.2 mL/h/L as observed by Chen et al. [187]. Nutrient broth and potato dextrose broth medium (H1 medium) was cultured using *Enterobacter cloacae* ATCC 13047 and *Kluyveromyces marxianus* 15D microbial after which cells were removed from the medium. The H1 medium and GAM broth medium were mixed and inoculated with the bacterial strain *Clostridium acetobutylicum* ATCC 824 to anaerobically produce biohydrogen.

Despite the various advantages of biohydrogen production, there exist certain disadvantages, which act as impediments in industrial scalability. Hydrogen storage, compressor and distribution networks and lack of durable fuel cell technologies are all technological barriers that need to be overcome. In addition to technological barriers, pretreatment of biomass waste and the cost of producing biohydrogen being more expensive than traditional fuels are drawbacks that need to be addressed [184].

9. Prospects for biohydrogen production

Despite numerous studies showing feasible strategies for biohydrogen production, a leap to commercialization remains practically unattainable. Such a situation is a direct result of a long-standing gap between researchers and engineers [188]. For scientists to enlist the perspective of the industrial sector, they need to work towards an economic output, readily consumable by industry. Several studies have offered alternative approaches to biohydrogen generation from an economic standpoint. For instance, Sinha and Pandey [21] suggested identification of novel hydrogenases and metabolic pathways through genetic engineering, high-throughput genomic sequencing, environmental genomics and/or metagenomic technologies to significantly improve hydrogen yields. Additionally, certain downfalls in the elementary biohydrogen production process have resulted in a growing trend towards integrated methods of production. Nevertheless, critical concerns pertaining to the feasibility of establishing two coincident bioreactors may prove to be a daunting process. It has been suggested that broadening the scope of microorganisms which could complement each other (e.g. dark and photofermentative bacteria) might support the combined biohydrogen production strategies [189].

Integrated approaches present promising results with the added advantage of reducing environmental externalities of generated waste. For instance, Liu et al. [81] devised a novel technique to overcome complications in biohydrogen production. A solar fluidized tubular photocatalytic reactor (SFTPR) with a simple and efficient light collector was proposed, which could simultaneously degrade waste activated sludge and produce hydrogen. The inner walls of the glass tubes of the SFTPR were coated with the photo catalyst AgX/TiO_2 and production of

7866 μmol H_2/L-sludge was attained. Such combined systems open up a path for highly efficient and cost-effective generation of biohydrogen, despite the need for consistent research to standardize the process to its optimal throughput. To this end, for example, Prieto et al. [190] fabricated a novel composite bioactive membrane coated with encapsulated acetogenic bacteria to concomitantly generate and capture hydrogen during wastewater treatment process. Results exhibited a fair yield and a capture capacity of 19.2±3.0 mL H_2/g hexose (0.14±0.02 mol H_2/mol hexose); 99.1±0.2%, and 46.0±15.5 mL H_2/g hexose (0.34±0.12 mol H_2/mol hexose) and 79±19%, respectively when run with the feeds of sugar beet wastewater and dairy production wastewater. However, this type of protocol is at its infancy and demands more research for effective optimization and utilization. Likewise, Jawed et al. [191] demonstrated the possibility of producing 10 mol H_2/mol glucose compared to only 4 mol generated via dark fermentation biohydrogen production. Such a feat was the result of the successful adoption of versatile bioinformatics tools. In depth knowledge of the distinctive characteristics that bioinformatics and biotechnology offer is important for procuring higher yields and to resolve potential mishaps faced during the scaleup process.

A few other aspects also need to be considered for absolute biohydrogen generation. Firstly, the conversion of industrial wastewater/sludge into biohydrogen must be designed without the release of any effluent as this would detract from the ultimate goal of turning all waste to energy. Secondly, purification and separation technologies for capturing hydrogen need to be devised for microbial strains producing both methane and biohydrogen. More importantly, the design of reactors for hybrid biohydrogen production must be done in a way which harmonizes both processes, and minimizes the constraints posed when merged together.

Penultimately, herein, a sequential analysis is envisioned, with an initial characterization followed by extracting biohydrogen using a combination of effective pretreatment methods for complex industrial wastewater. With the inclusion of a bioinformatics approach to demonstrate pilot studies, the effective scaling up of the process can be achieved (Fig. 5). Such concepts can offer economic benefits without compromising valuable environmental resources.

10. Hydrogen-fueled economy: The future of global energy

Hydrogen is primarily derived from fossil fuels and renewables, namely, solar, wind, hydro, biomass and geothermal. Production has even used waste sources over the past few decades, as illustrated in Fig. 6. Hydrogen can be produced from either one or all of these sources and is the simplest elemental material. However, hydrogen by nature is associated with both organic (combined with carbon as petroleum, natural gas or coal) and inorganic materials (e.g. water) reflects a critical challenge with respect to its production from naturally occurring matter. Among the several methods for the generation or extraction of hydrogen, steam reformation is perhaps the best established; it produces hydrogen from hydrocarbons/water. (Ninety-five percent of global hydrogen is produced by steam reformation). Electrolysis is also being used for deriving hydrogen through the decomposition of water by passing electric current (generated from various renewable/non-renewable sources). In order to effectively optimize the various processes for biohydrogen generation, the economy of hydrogen production exists as the most crucial factor to be assessed. At present, the cost of steam-reformation-based hydrogen production is 18 USD/million BTU, which is three times higher than the cost of natural gas (~6 USD/million BTU). The cost of hydrogen production from electrolysis is ~28 USD/million BTU, and is a linear function of electricity prices. Such market aspects emphasize the need for a waste-based hydrogen economy to be established in order to overcome the biggest electricity/energy barrier and nurture a sustainable development with greater energy security.

There are certain key drivers that can affect a clean and green hydrogen economy. For the end use of hydrogen, four elements are essential (Fig. 7) including (1) preparation of feedstocks for smooth and efficient processing, (2) hydrogen processes, (3) purification of hydrogen from contaminants by downstream processing, and (4) hydrogen distribution and storage. For a clean hydrogen economy, all these four elements need to be emphasized equally. This paper addresses the first element while several field trials are necessary for the others. Industrial applications are possible only when the above-mentioned four elements are addressed together. For industrial applications, the product needs to be technically viable, economically feasible and should reduce environmental impacts [192, 193]. Certain key technical achievements include the in-depth understanding of the pretreatment mechanisms and reactions. However, cost-effective pretreatments without any inhibitor formation are still under evaluation. New technologies such as single-pot systems and combined bioprocessing assist in reducing the costs of technology. Metallic organic frameworks are viewed as possible options for hydrogen storage and significant advancements have been achieved in the last decade.

11. Conclusions

Biohydrogen production using agro-industrial waste materials and effluents with a combination of pretreatment methods has an immense potential to meet the present-day energy demands and for ensuring future energy security. Innovations in the fields of economic biohydrogen generation, optimization of feedstock processing through various pretreatments and unique biohydrogen storage principles are the need of the hour for complete replacement of fossil-based energy sources. Despite showing higher biohydrogen production rates, integrative pretreatment approaches also need to be evaluated on the economic front in order to gain a strong foot in the field of energy generation. Moreover, it is apparent that the agricultural waste is more popular than industrial effluents for bioenergy generation. Research utilizing prominent and harmful industrial effluents as substrates is likely to incur more novel beneficial outcomes on the environmental front. Moreover, it is of supreme importance to fabricate large scale biohydrogen production processes inclusive of pretreatment technologies with little or no generation of secondary pollutants or effluents. Therefore, it is envisioned to build sustainable and large scale biohydrogen reactors with a complete biorefinery approach, transforming all wastes into a valuable energy resource for a sustainable hydrogen-driven economy.

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Figure legends

Figure 1. Intracellular pathways for biohydrogen production involving essential metabolites and processes

Figure 2. Biohydrogen production routes a) Biophotolysis b) Photofermentation c) Dark fermentation and d) Microbial electrolysis

Figure 3. Factors affecting biohydrogen production

Figure 4. Various pretreatments for sustainable hydrogen production from agro-industrial waste

Figure 5. Steps involved in the setup of algae-scale biohydrogen production plant

Figure 6. Hydrogen economy for a sustainable future

Figure 7. Factors involved in using hydrogen as fuel for the future

Figure. 1

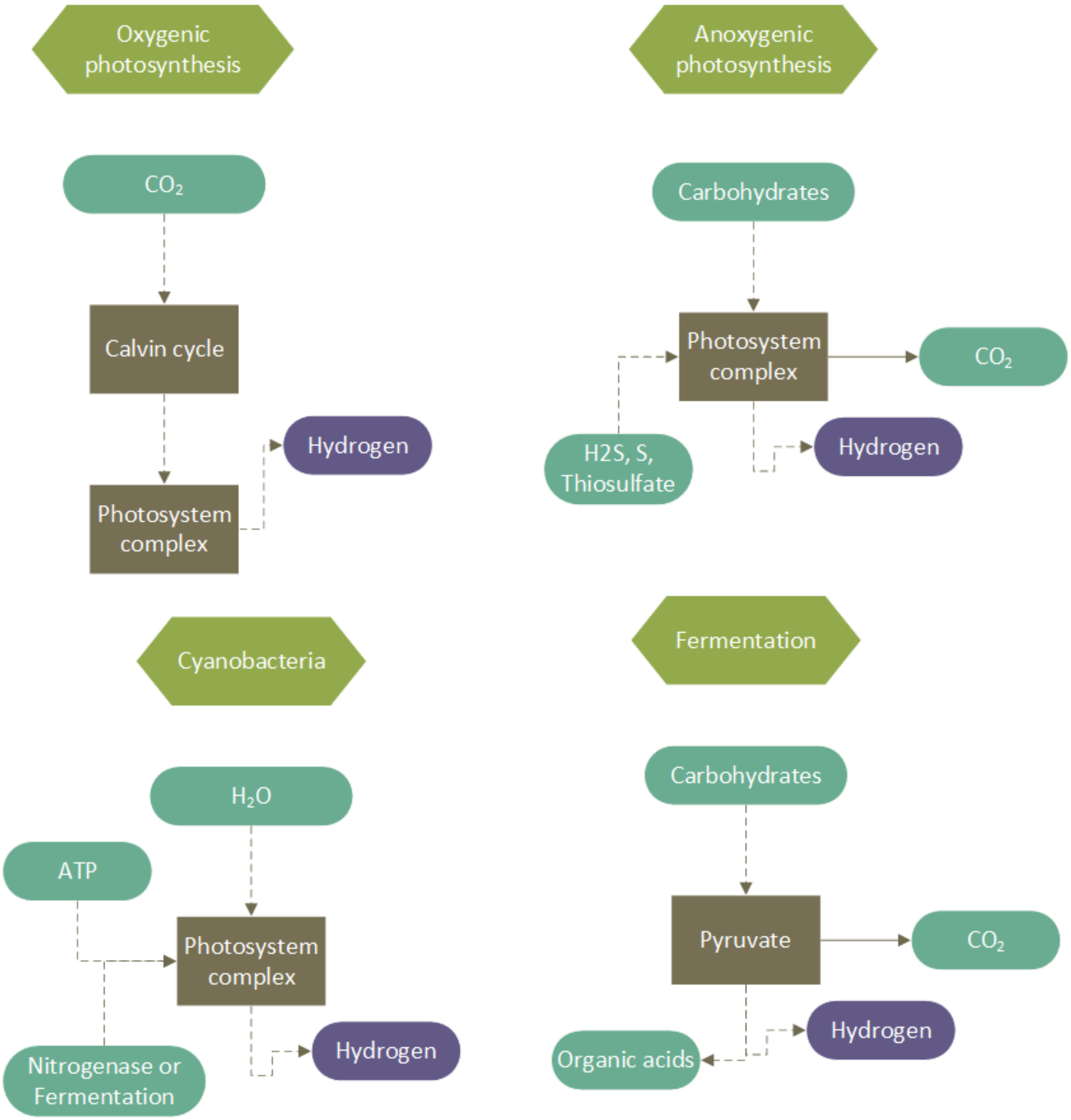
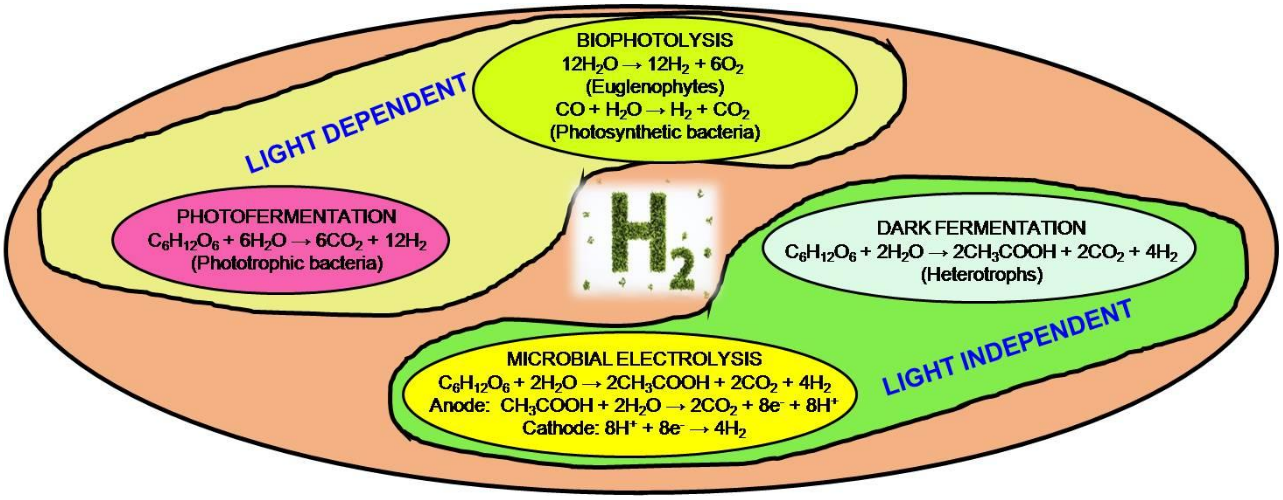

Oxygenic photosynthesis
CO_2
Calvin cycle
Photosystem complex
Hydrogen
Anoxygenic photosynthesis
Carbohydrates
Photosystem complex
CO_2
H2S, S, Thiosulfate
Hydrogen
Cyanobacteria
H_2O
ATP
Photosystem complex
Nitrogenase or Fermentation
Hydrogen
Fermentation
Carbohydrates
Pyruvate
CO_2
Hydrogen
Organic acids

Figure. 2



BIOPHOTOLYSIS
$12H_2O \rightarrow 12H_2 + 6O_2$
(Euglenophytes)
$CO + H_2O \rightarrow H_2 + CO_2$
(Photosynthetic bacteria)
LIGHT DEPENDENT
PHOTOFERMENTATION
$C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 12H_2$
(Phototrophic bacteria)
H_2
DARK FERMENTATION
$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2$
(Heterotrophs)
LIGHT INDEPENDENT
MICROBIAL ELECTROLYSIS
$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2$
Anode: $CH_3COOH + 2H_2O \rightarrow 2CO_2 + 8e^- + 8H^+$
Cathode: $8H^+ + 8e^- \rightarrow 4H_2$

Figure. 3

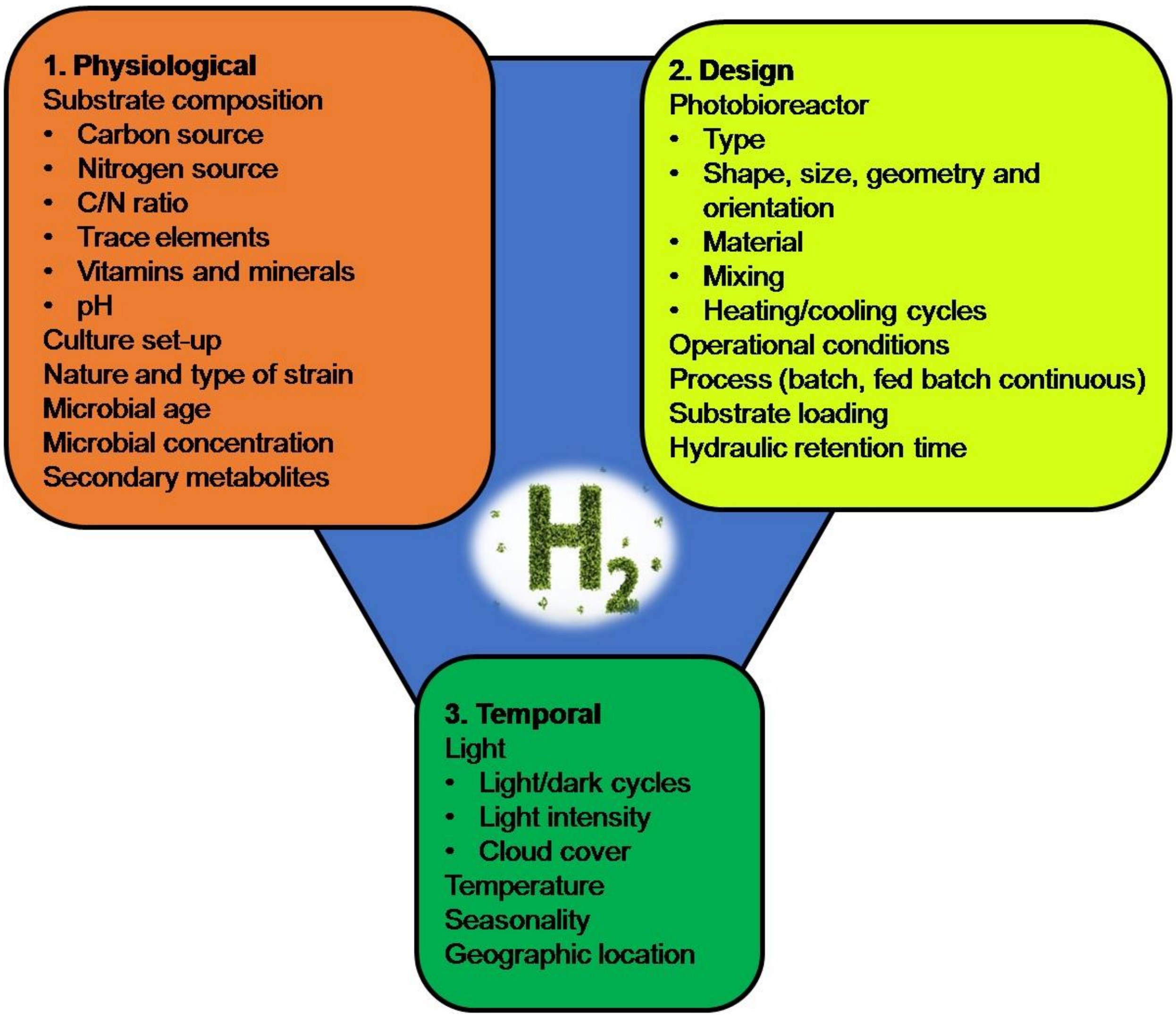
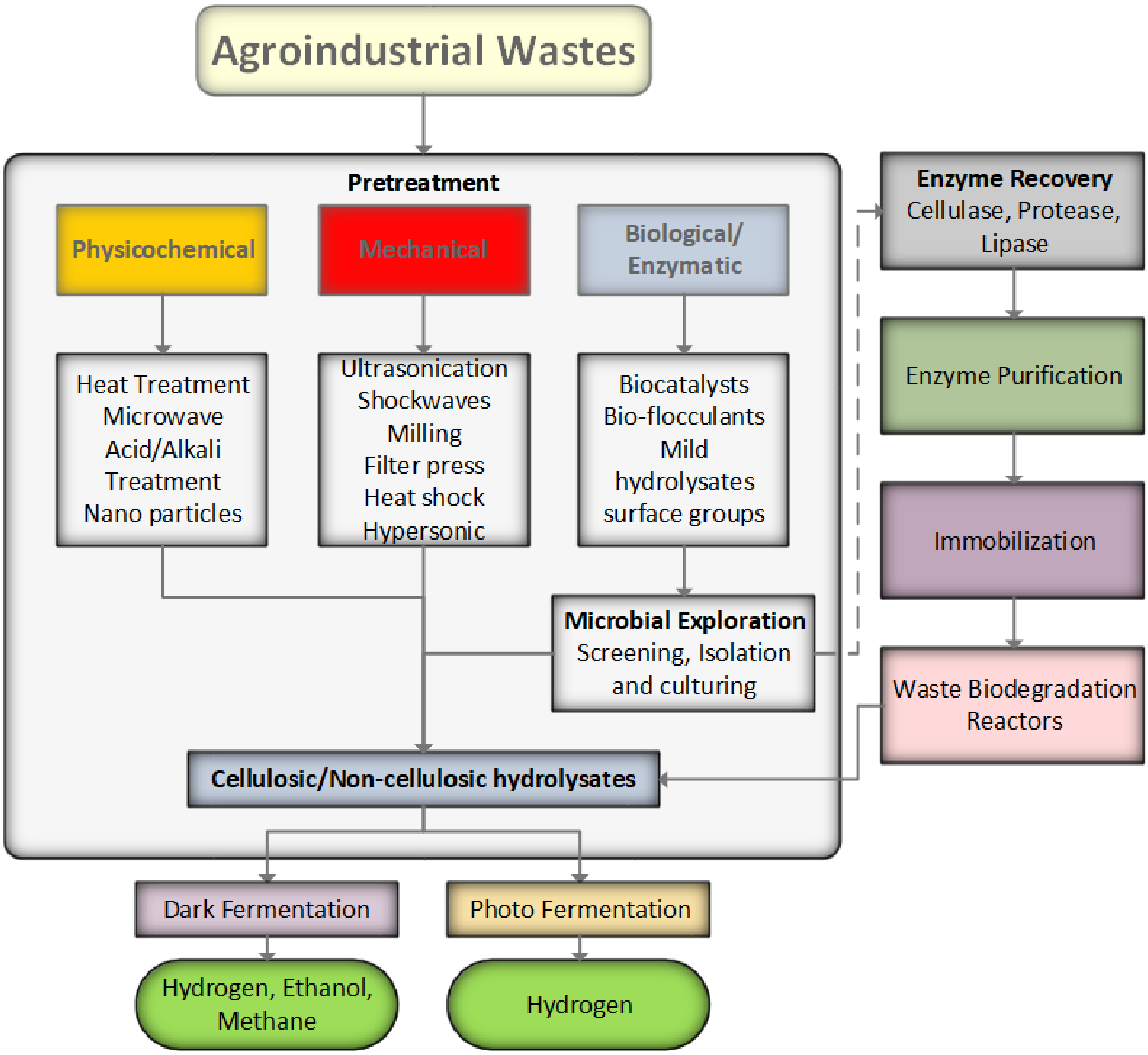
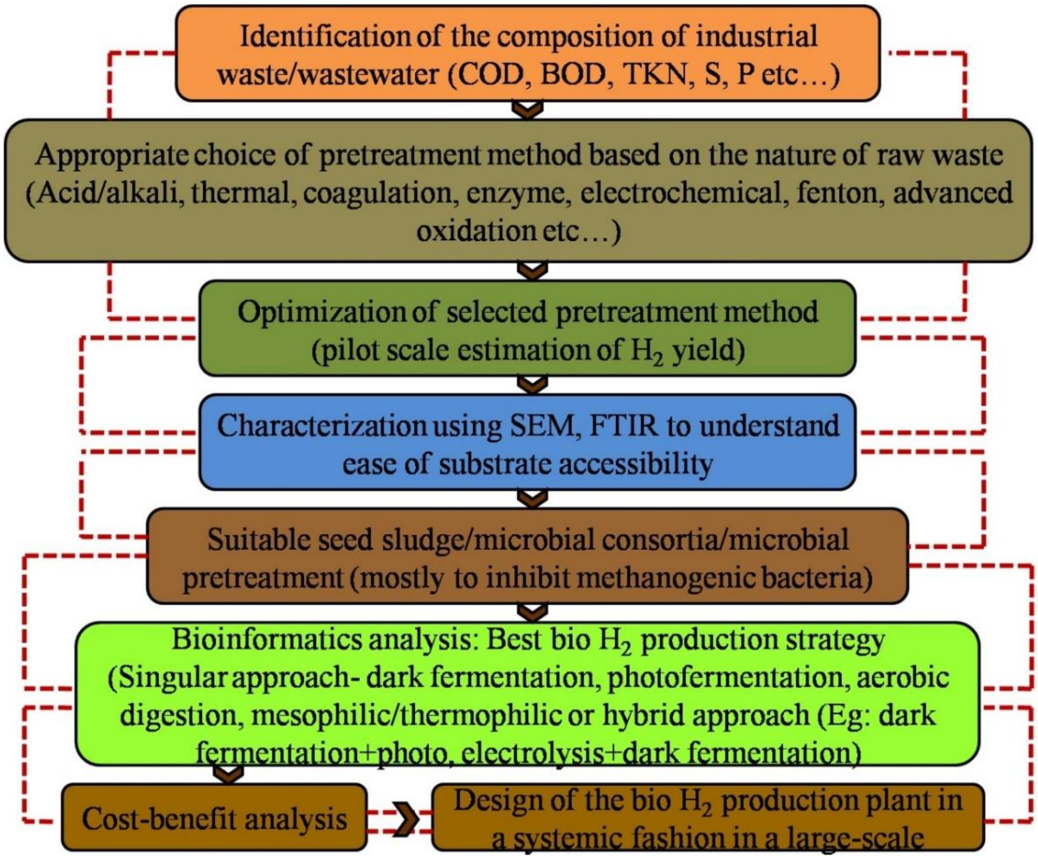

1. Physiological
Substrate composition
• Carbon source
• Nitrogen source
• C/N ratio
• Trace elements
• Vitamins and minerals
• pH
Culture set-up
Nature and type of strain
Microbial age
Microbial concentration
Secondary metabolites
2. Design
Photobioreactor
• Type
• Shape, size, geometry and orientation
• Material
• Mixing
• Heating/cooling cycles
Operational conditions
Process (batch, fed batch continuous)
Substrate loading
Hydraulic retention time
H2
3. Temporal
Light
• Light/dark cycles
• Light intensity
• Cloud cover
Temperature
Seasonality
Geographic location

Figure. 4



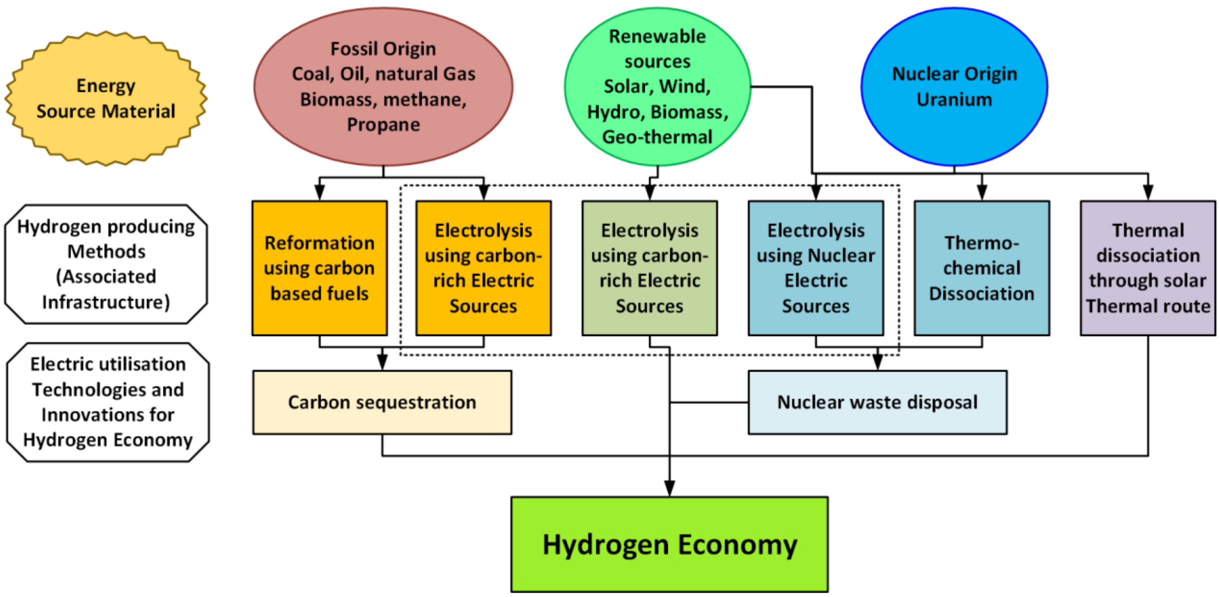
Agroindustrial Wastes
Pretreatment
Physicochemical
Mechanical
Biological/ Enzymatic
Heat Treatment
Microwave
Acid/Alkali Treatment
Nano particles
Ultrasonication
Shockwaves
Milling
Filter press
Heat shock
Hypersonic
Biocatalysts
Bio-flocculants
Mild hydrolysates
surface groups
Microbial Exploration
Screening, Isolation and culturing
Cellulosic/Non-cellulosic hydrolysates
Enzyme Recovery
Cellulase, Protease, Lipase
Enzyme Purification
Immobilization
Waste Biodegradation Reactors
Dark Fermentation
Photo Fermentation
Hydrogen, Ethanol, Methane
Hydrogen

Figure. 5



Identification of the composition of industrial waste/wastewater (COD, BOD, TKN, S, P etc…)
Appropriate choice of pretreatment method based on the nature of raw waste (Acid/alkali, thermal, coagulation, enzyme, electrochemical, fenton, advanced oxidation etc…)
Optimization of selected pretreatment method (pilot scale estimation of H2 yield)
Characterization using SEM, FTIR to understand ease of substrate accessibility
Suitable seed sludge/microbial consortia/microbial pretreatment (mostly to inhibit methanogenic bacteria)
Bioinformatics analysis: Best bio H2 production strategy (Singular approach- dark fermentation, photofermentation, aerobic digestion, mesophilic/thermophilic or hybrid approach (Eg: dark fermentation+photo, electrolysis+dark fermentation)
Cost-benefit analysis
Design of the bio H2 production plant in a systemic fashion in a large-scale

Figure. 6



Energy Source Material
Hydrogen producing Methods (Associated Infrastructure)
Electric utilisation Technologies and Innovations for Hydrogen Economy
Fossil Origin Coal, Oil, natural Gas Biomass, methane, Propane
Renewable sources Solar, Wind, Hydro, Biomass, Geo-thermal
Nuclear Origin Uranium
Reformation using carbon based fuels
Electrolysis using carbon-rich Electric Sources
Electrolysis using carbon-rich Electric Sources
Electrolysis using Nuclear Electric Sources
Thermo-chemical Dissociation
Thermal dissociation through solar Thermal route
Carbon sequestration
Nuclear waste disposal
Hydrogen Economy

Figure. 7

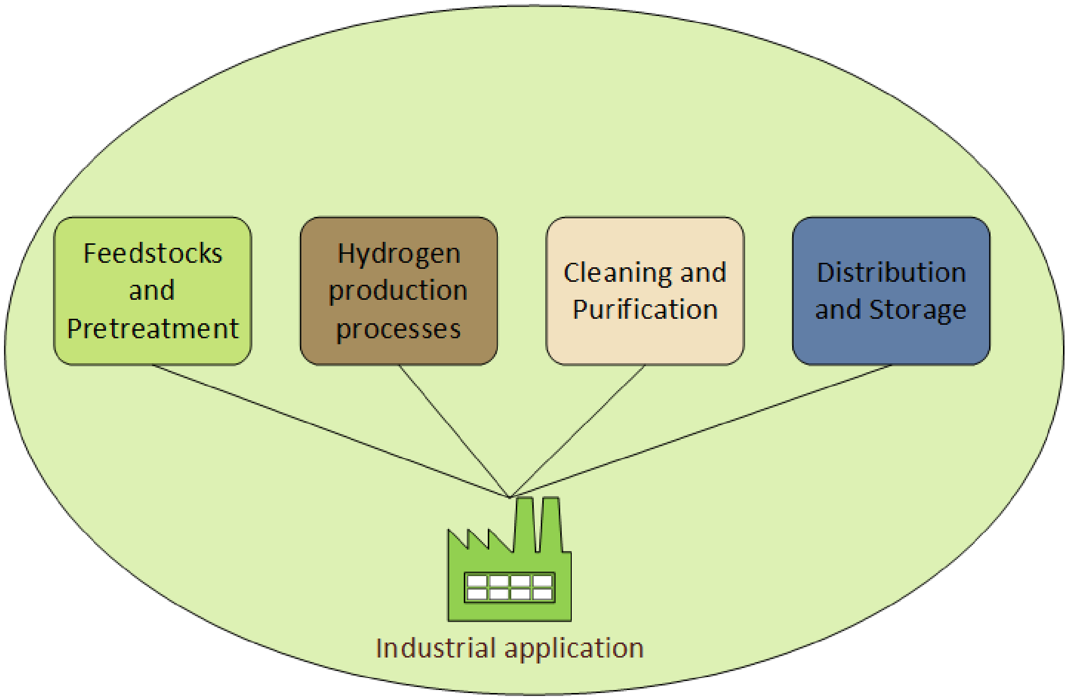

Feedstocks and Pretreatment
Hydrogen production processes
Cleaning and Purification
Distribution and Storage
Industrial application

Table 1

Table 1: Various influencing parameters on biohydrogen production using wastewater

S. No	Parameter studied	Influence on biohydrogen production	Vital inferences	References
1.	Effect of carbonate and phosphate (NH_4HCO_3, Na_2HPO_4 and Na_2CO_3)	Concentration dependent (Optimum Na_2HPO_4 concentration was 600 mg/L)	Phosphate shows better-buffering capacity than carbonate	[25]
2.	N_2 sparging	68% increase in hydrogen yield	Hydrogen partial pressure in the liquid phase is important	[26]
3.	Heat pretreated mixed inoculum	98.8 % of hydrogen in total biogas produced	Heat can eliminate hydrogen-consuming bacteria/methanogens	[27]
4.	Substrate concentration	Peak hydrogen of 1154 ±26 mL at of 8 g COD/L wastewater	Excessive substrate concentration result in the acidification of system and accumulation of VFA	[28]
5.	Inoculum concentration	Hydrogen yield of 104.58 mL H_2/g-VS_{added} for 2.30 g-VSS/L of inoculum concentration	The presence of *Lactobacillus* sp. and *Enterococcus* sp. might be responsible for the low HY and SHPR	[29]
6.	Combination of BW and pulp and paper mill effluent (PPME)	Reuse of the BW and PPME resulted in 42.3 and 44.0 % less hydrogen yields	Improved nutrient and light penetration into the medium	[12]
7.	Organic loading rate (OLR)	Hydrogen increased (95.5 to 117 mmol/d), with increasing OLR	Total VFAs production varies consistently with the OLR	[30]

		(7.1 to 21.4 g COD/L d) then dropped		
8.	CSTR and UASBr	Maximum hydrogen yield of 1.29 mol H_2/mol $hexose_{added}$ using UASBr	Non-hydrogenic, lactic acid was dominant in CSTR, while butyric and caproic acids in UASBR	[31]
9.	Effects of N/C, P/C and Fe/C ratios	0.656 mol H_2/mol glucose) at 0.05, 0.09 and 0.003 (w/w)	Low HY is caused by the presence of toxic chemicals (5- HMF), lack of essential micro nutrients and the composition of the inoculum	[32]
10.	Suspended and attached microbial growth systems	Maximum HPRs of CSTR (201.8 mL/(h·L)) and CMISR (255.3 mL/(h·L))	CMISR allows better biomass retention than CSTR	[33]

Table 2

Table 2. Various pretreatment methods and subsequent hydrogen yield under optimized conditions

S. No	Type of effluent	Pretreatment methods	Strains	Optimal conditions	Hydrogen production	Reference
1.	Solid organic matter in POME	Alkaline and Acid	*Thermoanaer-obacterium*	pH-5.5; temp-60 °C	5.2 L H_2/L- POME	[122]
2.	Raw food waste	Autoclave pretreatments	*Clostridium beijerinckii*	pH-7	38.9 mL H_2/g-VS_{added}	[123]
3.	Microalgal biomass	Novel enzymatic pretreatment	*Chlorella vulgaris*	CHEES (enzyme) extracted at 52 h	43.1 mL H_2/g dcw	[124]
4.	Diary effluent	Biological method	Bacteria B1 and B4	pH-5; temp-70 °C; Fe ion conc-100 mg/L	55±0.58 mL with HPR 5.729 mL/L/h at 24 h HRT	[125]
5.	Cheese whey	Hydrodynamic cavitation + Alkaline	—	pH-10; 20 kHz frequency	3.30 mol H_2/mol lactose	[126]
6.	De-oiled Jatropha waste	Heat pretreatment (90 °C, 30min)	*Clostridium* sp	pH-6.53; temp-55.1 °C	20 mL H_2/g VS (Volatile Solid)	[10]
7.	Agro-industrial waste	BESA (2-bromoethanesulfonic acid)	—	Temp-35±1 °C; pH-6.8 (fennel waste), 7.4 (buffalo manure)	Fennel wastes (58.1±30 mL H_2/g VS); buffalo manure (135.6±4.1 mL H_2/g VS)	[127]
8.	Sewage sludge	Alkaline pretreatment	*Eubacterium multiforme*	pH-11	9.1 mL H_2/g of dry	[128]

			and Paenibacillus polymyxa		solids	
9.	Anaerobic sludge	Heat treated (102 °C, 90 min)	__	pH-6.5; 25 g/L glucose conc	2.02 mol H_2/mol$_{glucose\ consumed}$	[129]
10.	Palm oil mill effluent (POME)	Autoclaved pretreatment	Engineered *E. coli* BW25113	Temp-37 °C with 24 h mild agitation	0.66 mol H_2/mol total monomeric sugar	[130]
11.	Sugar rich Cassava wastewater	Biological treatment	*Clostridium acetobutylicum*	pH-7-5; temp-36 °C	2.41 mol H_2/mol glucose	[131]
12.	Textile wastewater	Activated Carbon	*C. butyricum* and *K. oxytoca*	pH-7.0; temp-37 °C; substrate conc-20g sugar/L	1.37 mol H_2/mol hexose	[132]
13.	Rice mill wastewater	Combined acid + enzymatic hydrolyses	*Enterobacter aerogenes* RM08	Acid-1.5% sulfuric acid; temp-29 °C (enzyme)	1.97 mol H_2/mol of sugar	[133]
14.	Palm oil mill effluent	Heat-shock	Anaerobic mixed microflora	pH-5.5; temp-35 °C	0.41 mmol H_2/g COD	[134]
15.	Paper and pulp industry effluent	Enzymatic hydrolyses	*Enterobacter aerogenes*	Temp-29 °C; sugar conc-22 g/L total sugar	2.03 mol H_2/mol sugar	[79]
16.	Beet-pulp	Alkaline pretreatment	Anaerobic mixed microbes (sludge)	pH-6; temp-35 °C±2	115.6 mL H_2/g COD	[135]
17.	Soluble condensed	Heat treatment (100 °C, 45 min)	*Clostridium* sp.	pH-5.5; temp-35 °C; HRT-3 to 24 h	390 mmol H_2/L/d	[136]

	molasses					
18.	Cassava wastewater	Enzymatic (alpha-amylase)	—	pH-7.0; temp-105 °C	5.02 mol H_2/g COD	[106]
19.	Textile designing wastewater (TDW)	Coagulation 1 g/L	Seedmicroflora (sludge from methane digester)	pH-6.8; temp-35 ˚C TDW conc of 15 g total sugar/L	1.52 mol/mol hexose	[14]
20.	Rice straw hydrolysate	Acid Con H_2SO_4 (55%) of 40 ˚C.	Municipal seed sludge (heat 95-100 ˚C for 1h)	pH 7; temp-37 ˚C	0.44 mol H_2/mol T-sugar	[81]
21.	Sunflower stalks	Two-stage alkaline-enzymatic pretreatment	Anaerobically digested sludge washeat shocked (90 °C, 15 min)	Temp-170 ˚C	59.5 mL H_2/g initial VS	[137]
22.	Waste activated sludge	TiO_2 photocatalysis 5.0 mg/L under 2.4 w·m−2 UV	Acid pretreated sludge	pH-7; temp: 35 ˚C	11.7 mL H_2/g-VS	[116]
23.	Cotton plant stalk waste	80 °C for 12 h by 4% (w/w) ammonia solution	Mixed culture (Wastewater Treatment sludge) was heat-shocked at 85 °C for 45 min	Mesophilic conditions (37 °C)	15.2 mL/g VS	[138]
24.	Probiotic wastewater	heat treated at	Sludge from slaughter house manure 85˚C for	pH-5.5; substrate conc-5 g/L	1.8 mol H_2/mol carbohydrate	[139]

		50 ˚C for 10 min	1 h and acid treatment at a pH of 3–4 for 24 h			
25.	Waste activated sludge from sewage treatment plant	Combined ozone/ultrasound	Sludge heated at 90 ˚C for 15 min in awater bath	Ozone dose of 0.158 g O_3/g DS and ultrasound energy the density of 1.423 W/mL	9.28 mL H_2/g DS	[140]

***Highlights**

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- This review focused on biohydrogen production using pretreated industrial waste
- Improved biohydrogen production using various pretreatment technologies
- Discussed the future prospects on sustainable biohydrogen economy.