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Biohydrogen production from industrial wastewater: An overview

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ABSTRACT

Biohydrogen production from industrial wastewater has been a focus of interest in recent years. The in depth knowledge in lab scale parameters and emerging strategies are needed to be investigated in order to implement the biohydrogen production process at large scale. The operating parameters have great influence on biohydrogen productivity. With the aim to gain major insight into biohydrogen production process, this review summarizes recent updates on dark fermentation, inoculum pretreatment methods, operating parameters (hydraulic retention time, organic loading rate, pH, temperature, volatile fatty acids, bioreactor configuration, nutrient availability, partial pressure etc.). The challenges and limitations associated with the biohydrogen production are lack of biohydrogen producers, biomass washout and accumulation of metabolites are discussed in detail. The advancement strategies to overcome these limitations are also briefly discussed.

1. Introduction

About 87% of energy consumption is achieved by using fossil fuel as a major source (Xia et al., 2016). Hydrogen is considered to be one of the alternative source which can be derived from renewable and sustainable source of energy (Plangklang et al., 2012). The hydrogen is a sustainable fuel which generates water and energy, it overcomes the negative effects from the usage of fossil fuels (Poleto et al., 2016). The economic and promising way of producing biohydrogen is using microbes under dark or photo fermentation methods (Argun and Dao, 2017). Several researchers worked with the industrial wastewater from sugar industry, beverage industry, chemical industry, palm oil effluent, distillery industry effluent as substrate for the biohydrogen production (Boodhun et al., 2017). In acidogenic phase of an anaerobic digestion the hydrogen is produced as a by-product and the yield is very low. The dark fermentation methods were established to enhance the production of hydrogen whereas it is a challenge towards commercial use (Kumar et al., 2017). The dark fermentative hydrogen production is improved by pretreating the substrate or inoculum. The pretreatment of inoculum were helpful in suppressing the activity of methanogens and increasing the activity of hydrogen producing bacteria (Venkata Mohan et al., 2008). The efficient and beneficial hydrogen productions by fermentation were influenced by various factors such as substrate composition, nutrient availability, mode and operation of reactors, bacterial consortium and its yield (Mota et al., 2018). The substrate is one of the important factors that are necessary for the metabolism of microbes involved in biohydrogen production and the yield can be increased by the optimization of carbon to nitrogen ratio (Hernández-Mendoza et al., 2014). The optimisation of these factors helps in smooth flow of process of biohydrogen productions. In textile industry and pharmaceutical industry various toxic compounds were produced, which disturbs the overall hydrogen production process. Hydrogen production potential (HPP) are evaluated to know the amount of inhibitory compounds (Lay et al., 2012; Chu et al., 2013). The advancement and the modifications of various factors through technological means help to move towards commercialisation. The technical and economical issues like storage, distribution and expensive infrastructure are the major barriers for commercialisation. The recent progress in large scale hydrogen producing technologies may overcome the technical and commercial issues (Singh and Rathore, 2017). This review article summarizes the various research work carried out in biohydrogen production using industrial wastewater as substrate and various operational parameters which affects the effective hydrogen productions were compared. The major limitation and challenges in biohydrogen production and the advancement in technologies to overcome the issues in large scale biohydrogen production were discussed in detail.

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1.1. Dark fermentation

The anaerobic fermentation in absence of light breaks down the carbohydrate to form hydrogen and other intermediates called dark fermentation and the intermediate compounds like volatile fatty acids (VFA) and alcohols were also produced. Bacteria such as *Clostridia* sp., and *Enterobacter* sp. were used for dark fermentation of carbohydrates (Levin et al., 2004). The anaerobic metabolism of pyruvate accelerates the hydrogen production, formate lyase and ferredoxin oxido reductase enhances the breakdown of pyruvate. The main factors like temperature, pH, substrate, nutrition feed etc. should be maintained for efficient biohydrogen production especially, the pH affects the hydrogenase enzyme activity. In a study by Ginkel et al. (2005), the pH was maintained at 5.5–8 to enhance the production of biohydrogen by 60–70%. In a study by Van Niel et al. (2003) the effect of hydrogen inhibitors were studied and shows that the lactate, ethanol, acetate etc. are the major products which inhibit biohydrogen production. Ozmihci and Kargi (2011) used *Clostridium butyricum* for continuous production of biohydrogen using wheat starch in dark fermentation.

2. Pretreatment of inoculum

In hydrogen production the pretreatment allows us to select the group of acidogenic bacteria (AB) and thereby inhibiting the methanogenic bacteria (MB) in mixed culture. The hydrogen producing bacteria i.e. AB can produce a layer surrounds its cell surface which protects it from severe environmental conditions whereas the hydrogen consuming bacteria i.e. MB lacks this capacity (Zhu and Beland, 2006). The untreated biocatalysts have wide range of microorganisms with different metabolic activities. The pretreatment helps us to select the microorganisms having the biochemical function towards acidogenesis. Pretreatment of inoculum helps to reduce the substrate degradation which attributes to the inhibition of hydrogen consuming bacteria (Srikanth et al., 2010).

2.1. Physical treatment

This treatment involves the physical forces to treat biomass without any actions of chemical and enzyme (Zheng et al., 2014). The physical treatment mainly includes microwave and thermal treatment. Microwave pretreatment inactivates the microorganisms through thermal and non-thermal effect.

Microwave pretreatment is the irradiation of electromagnetic waves of 300 MHz to 300 GHz frequency which produces heat in liquids and it disrupts the cell wall of biomass and increases the solubility of the medium. The rearrangement of dipoles due to the heat generated is the reason for disruption (Banik et al., 2003). It inactivates the non-hydrogen producer by extracting the contaminant in inoculum which causes adverse effect to hydrogen producers. In mixed culture, the *Clostridium* sp. was found to be dominated, when it is pretreated with microwave (Singhal and Singh, 2014; Guo et al., 2015).

Heat shock treatment (HST) is a thermal treatment which helps for the growth of hydrogen producing bacteria which suppresses the activity of methanogens. The spore formation indicates the hydrogen producing bacteria and in this treatment the non sporing bacterium were killed i.e. the methanogens and the non sporulating hydrogen producing bacteria (Zhu and Beland, 2006). The parameters of HST will vary according to its temperature between 80 and 104 °C and exposure time between 15 and 120 min (Zhu and Beland, 2006). The HST treatment in batch reactor with mesophillic conditions encourage to produce more hydrogen. The hydrogen yield (HY) of 2.49 mol H_2/mol hexose were found by using anaerobic sludge as inoculum at 100 °C temperature and 60 min treating time (De Sa et al., 2013). The microwave treatment shows higher efficiency than the thermal treatment in terms of cell solubilisation when compared under same temperature (Kuglarz et al., 2013).

2.2. Mechanical treatment

Ultrasonication is a wave when propagates in the medium, forms bubbles which when collapse produce highly active radicals, shear force, high temperature and pressure (Wang et al., 2010). The input energy control in inoculum helps to suppress the methanogens and protects the hydrogen producing bacteria (Dhar et al., 2012). The ultrasonic pretreatment of *Rhodopsuedomonas palustris* QK01 increased the biohydrogen yield by 66.7% (Hay et al., 2016). In an investigation by Budiman et al. (2017) the HY was increased to 14.438 ml H_2/mL $_{\text{medium}}$ when the inoculum *R. sphaeroides NCIMB8253* was pretreated with ultrasonicator for 10 min.

2.3. Chemical treatment

In chemical treatment process the Acetylene, iodopropane, 2 - Bromo ethanesulfonic acid (BESA) served as inhibitors for hydrogen consuming bacteria. The treatment with BESA facilitates the destruction of methanogens without disturbing the hydrogen producing bacteria. Iodopropane restricts the functioning of B12 enzyme which carries methyl group (Zhu and Beland, 2006). Acetylene has the ability to disturb the metabolic pathway of methanogens and declines the methanogenic functions (Valdez- Vazquez et al., 2006; Chan and Parkin, 2000). Acid treatment was used to kill MB which survives at narrow pH range and thereby protects the acidogenic bacteria which can survive at drastic range of pH (Oremland, 1998). The pH ranges between 5 and 5.5 provides an efficient hydrogen production by suppressing the activity of methanogens (Zhu and Beland, 2006). The acid treated inoculum shows higher biohydrogen production according to Chang et al. (2011), whereas the base treated inoculum shows higher HY due to the difference in microbial distribution as investigated by Yin et al. (2014) and Zhu and Beland (2006).

2.4. Biological pretreatment

The biological pretreatment employs bacteria or enzymes to increase the hydrolysis rate by breaking the bonded structures in wastewater. Enzymatic treatment is an option for the other types of biomass pretreatment. The reaction takes place under mild conditions without any formation of toxic products (Verardi et al., 2012).

Apart from these treatment processes the freezing thawing, infrared, forced aeration also provides efficient treatment. In forced aeration the anaerobic sludge will be inoculated with aerated sludge to suppress the activity of methanogens (Terentiew and Bangley, 2003). The infrared and freeze thaw treatment provides efficient removal of methanogens (Wang et al., 2003). In freezing and thawing the extreme changes in temperature leads to the intracellular formation of ice crystals take place and it leads to the disruption of microbial cells (Sawicka et al., 2010). In some cases the single pretreatment methods were not so effective to eliminate the methanogens and combined treatments are required to increase the efficiency to much higher level. The thermal treatments are widely used in case of combined pretreatment. Mohan et al. (2008) investigated the combination of heat shock with acid treatment and achieved higher HY as compared to single method. They also observed the inhibition of hydrogen production when heat shocks are combined with other chemical treatment. Boboescu et al. (2014) investigated the negative effect of combined pretreatment on HY as the irreversible deterioration of all the microbes and mainly the hydrogen producers.

3. Factors affecting biohydrogen production

The factors which affect the production of Biohydrogen were more likely to be the pH, temperature, organic loading rate (OLR), Hydraulic retention time (HRT), nutrient composition, partial pressure, metabolite concentration, mode and operation of reactors and substrate used for fermentation.

3.1. pH

pH is a crucial parameter which affects the efficiency of hydrogen production. The decrease in pH eventually affects the growth and the metabolic production of bacteria. The pH ranges 4.5–9 are considered to be efficient for biohydrogen production (Stavropoulos et al., 2016). The cumulative hydrogen production rate (CHPR) and HY have some influence due to change in pH and the hydrogen accumulation is completely dependent on pH and pH varies inversely with the HY (Silva et al., 2019). The pH at 5 reduces the hydrogen production due to lesser biomass growth and the effective production of hydrogen takes place above 5.5 pH (Sivagurunathan and Lin, 2019). Lower pH affects the activity of hydrogenase enzymes and inhibits the action of hydrogen producers (Liu et al., 2008; Ngo et al., 2012). At extreme pH conditions, the sporulating hydrogen producing microorganisms can survive whereas the methanogens will be eliminated (Shida et al., 2009). As contrast to certain literatures methane generation were also possible at low pH (Silva and Eyng, 2013; Hernández-Mendoza et al., 2014). The pH plays a major role in limiting the growth of bacteria and also shows the total solvent concentration. The optimum pH for high production of hydrogen and lower solvent production are between 5.5 and 6.5 (Ma et al., 2015).

3.2. Temperature

Temperature plays a major role since the substrate degradation, hydrogen production, growth of microorganisms and by products are dependent (Perna et al., 2013). The different temperature ranges in anaerobic fermentation are: ambient (15–30 °C), mesophillic (30–49 °C), thermophilic (50–64 °C), hyperthermophilic (65–80 °C), extreme thermophilic (> 80 °C). The mesophillic temperature of 30–49 °C is efficient for hydrogen production using mixed culture (Lin et al., 2012) and also favourable in terms of expense and technical features (Vatsala et al., 2008). The fermentative hydrogen productions are effective between 25 and 60 °C (Rosa et al., 2014). Hydrogen production and substrate degradation can be achieved efficiently at higher temperature with negligible energy recovery whereas the energy recovery was possible only at ambient temperature (Mu et al., 2006). The temperature shows opposite effect towards biogas solubility and therefore the connection between the microbes and the biogas in reactor will be smaller and it leads to the consumption of hydrogen produced by methanogenic and acetogenic bacteria (Silva et al., 2019). The increase of temperature from optimum limit leads to degradation of enzymes involved in hydrogen production process (Hernández-Mendoza et al., 2014). In brewery wastewater the increase in temperature from 25 to 40 °C increases the cumulative hydrogen production (CHP) yield and above 45 °C the production rate was affected. The thermophiles can be used when the mesophiles lack the tendency to use cellulose for hydrogen production directly (Dippolito et al., 2010). The hydrolysis rate will be high using thermophiles (Singh et al., 2015). In mesophiles, *Clostridium* and *Enterobacter* sp. shows higher hydrogen production rate (HPR) whereas in thermophiles *Thermobacterium* sp. shows higher yield. Thermodynamically, higher temperature favours hydrogen production due to increment in entropy of the system whereas in economic point of view extreme thermophiles conditions are not possible due to the energy required for maintaining temperature (Hallenbeck, 2005).

3.3. Hydraulic retention time

HRT or fermentation time is a parameter that influence on hydrogen production and evaluate the efficiency of produced gas. It is one of the eminent operating factors which restrict the methanogenic process during acidogenic fermentation. Longer HRT leads to the shift in metabolic activity from acidogenic to methanogenic phase, which eventually inhibits the production of hydrogen. Shorter HRT inhibits the action of methanogens (Hawkes et al., 2007). The shorter HRT less than the growth of slow growing microorganisms' i.e. methanogenic bacteria lead to washout of microorganisms (Ueno et al., 2001). The washout of methanogens helps to reduce the cost and size of reactors (Hawkes et al., 2007). The activity of methanogens can be restricted at the HRT of 2–10 h and the acidogenic bacteria will be increased (Zhu and Beland, 2006; Fang and Liu, 2002; Venkata Mohan, 2009).The optimum HRT for hydrogen production is maintained between 8 and 14 h (Chen and Lin, 2003; Liu and Fang, 2002; Hussy et al., 2003). The wastewater from dairy, chemical industries etc. used as a substrate for acidogenic activity can produce hydrogen at 0–14 h (Vijaya Bhaskar et al., 2008). The mixed cultures have the ability to continuously produce hydrogen for 3 days without any methanogenic inhibition. The HRT for hydrogen gas generation from dark fermentation occurs at 0.5 h–24 h depending upon the substrate and the process used (Fernandes et al., 2013; Singh et al., 2013; Wu et al., 2007; Perna et al., 2013). The higher void in support particle from biomass leads to higher release of gas from liquid to head space (Fernandes et al., 2013; Lee et al., 2003). Long HRT leads to higher production of total VFA and causes inhibition (Lee et al., 2003). It is also related to the specific growth rate of organisms involved in hydrogen production, where the increase in growth rate leads to decrease in HRT. The HRT can be controlled by dilution rate in continuous stirred tank reactor (Singh and Das, 2018) and the optimum HRT can be determined based on the bioprocess used (Karaosmanoglu Gorgec and Karapinar, 2018). A study by Mahmod et al. (2018) investigated the effect of HRT on pal oil mill effluent and found that the highest HY of 2.45 ± 0.24 mol H_2/mol sugar was obtained at 6 h. The maximum yield was obtained at lower HRT since the bacterial culture can adapt to the high substrate availability because of the active metabolism.

3.4. Organic loading rate

The OLR have major influence on biohydrogen production. The total conversion of carbohydrate is inversely proportional to OLR in the reactor, which indicates the overload of organic content and affects the performance of the reactor. The highest HY was obtained at lower glucose feeding rate. The HY will be lower at increased OLR due to overloading of organic substrates (Kargi et al., 2012; Rosales-Colunga et al., 2012). The HY varies with the function of OLR and the higher yield meets by lowering OLR (Spers et al., 2013). In a study by Castillo et al. (2007) the positive effects of OLR were seen in hydrogen production, where the production rate and yield was 0.042 ± 0.008 L H_2 h^{-1} L^{-1} and 0.668 ± 0.002 mol H_2/mol Lactose at the highest OLR of 37 ± 1 kg COD/m^{-3}/d^{-1}. The increase in OLR increases the microbial diversity and thereby decreasing its HY (Silva et al., 2019). The hydrogen production can be enhanced by optimising HRT and OLR in continuous system and it is considered as a threshold factor (Kumar et al., 2016a, 2016b, 2016c, 2016d).

3.5. Composition of nutrients

The availability of nutrients is necessary for attaining optimum growth of microorganisms. The carbon, nitrogen, vitamins and trace metals helps to maintain the growth of microorganisms. Nitrogen serves as an important source for the growth and also enhances the hydrogen production. The inorganic salt like urea doesn't contribute in the production of hydrogen (Yokoi et al., 2001). The waste from cornstarch serves as an alternative and used as a peptone supplement (Yokoi et al., 2002). The stabilization of dark fermentation process is enhanced by carbon to nitrogen ratio (C/N ratio) and affects the productivity and HPR. The overall hydrogen production will be enhanced by optimum phosphate content (Lin and Lay, 2004). The increase in phosphate content alters the cellular reducers from production of hydrogen and

Table 1
Hydrogen yield in different types of Industrial Wastewater at different operating conditions.

Industrial wastewater types	Reactor	Inoculum	pH	Temperature (°C)	HRT	Substrate concentration (gCOD/l)	H_2 yield	Reference
Cassava wastewater	AFBR	Sludge from Swine wastewater treatment	5.00 ± 0.48	28 ± 2	2 h	4	1.91 mol H_2/mol glucose	Amorim et al. (2014)
Pulp and paper mill effluent	Batch	Anaerobic sludge	5	37	45 h	5	55.4 mL/g-COD	Vaez et al. (2017)
Paper mill wastewater	UASBR	Paper mill sludge	5	35	9.6 h	2.217 ± 0.169	1.22 ± 0.11 mmol/g COD initial	Farghaly et al. (2015)
Paper mill wastewater	UASBR	Mixed culture	5	35	9.6 h	2.217 ± 0.169	5.29 ± 0.16 mmol/g COD initial	Farghaly et al. (2015)
Rubber industry effluent	Batch	Pretreated mixed microflora	7	37	7 d	0.45	55.6 ml/g substrate	Murugesan and Bala Amutha (2010)
Alcohol industry wastewater	UASBR	Sludge from alcohol wastewater treatment plant	5.5	37	0.96 d	45	125.1 ml H_2/g COD removed	Poontaweegeratigarn et al. (2012)
Rice winery wastewater	UAR	Mixed anaerobic consortium	5.5	55	2 h	34	2.14 mol/mol-hexose	Yu et al. (2002)
POME	Two stage fermentation reactor	Anaerobic sludge	5.5	55	9 h	76.5 ± 0.3	49.22 ml H_2/g COD applied	Krishnan et al. (2016)
POME	Two stage fermentation reactor	Mixed culture	5.5–6.5	55	12 h	20	2.99 mol H_2/mol-sugar	Maaroff et al. (2018)
POME	Two stage fermentation reactor	Mixed culture	5.5–6.5	37	12 h	20	1.19 mol H_2/mol-sugar	Maaroff et al. (2018)
Soybean protein processing wastewater	ABR	Excess sludge (I & II reactor) and anaerobic granular sludge (III & IV reactor)	6.7	35 ± 1	48 h	1.83–2.4 (I & II reactor) and 3.86–5.10 (III & IV reactor)	25.67 l/d	Zhu et al. (2013)
Beverage wastewater	Batch	Mixed culture	5.5	37	96 h	20	3.76 mol H_2/mol-sucrose utilized	Sivagurunathan and Lin (2019)
Dairy industry wastewater	AFBR	Biomass from fermentation	3.7–4.3	24–30	8 h	8.12–15.44	2.56 mol H_2/mol carbohydrate	Silva et al. (2019)
Molasses wastewater	Batch	Pure culture *Enterobacter aerogenes*		30	24 h	40	6.02 mm/g sugar	Kumar et al. (2016a), (2016b), (2016c) and (2016d)
Brewery wastewater	Anaerobic batch reactor	Anaerobic granulated mixed consortium	5.5	37	180 h	2	1.5 mol H_2/mol fructose	Pachiega et al. (2018)

COD: chemical oxygen demand AFBR: anaerobic fluidised bed reactor UASBR: upflow anaerobic sludge blanket reactor UAR: upflow anaerobic reactor HRT: hydraulic retention time ABR: anaerobic baffled reactor.

thus VFA concentration increases and decrease the overall hydrogen production. Trace elements like Mg, Na, Zn, Fe, K, I, Co, Mn, Ni, Cu, Mo and Ca have certain effects on hydrogen production (Lin and Lay, 2004). The enzyme functioning can be enhanced by supplementing trace metals.

3.6. Volatile fatty acid concentration

The metabolic end product affects the HY in fermentative hydrogen production. The dominant metabolic products are acetic acid, ethanol, butyric acid and propionic acid (Lee et al., 2002). The number of hydrogen mole production depends on the type of metabolite and it serves as a crucial factor to analyse the total hydrogen produced. The metabolic route can be affected by HRT and OLR (Tchamango et al., 2010). The increment in VFA concentration leads to the lysis of the cells through the permeation of proton onto the cell membrane of sporing bacteria and thus disruption of cells takes place. The restoration of cell membrane takes place by maintenance energy which adjusts the growth of microorganism and enhances hydrogen production. The substrate degradation efficiency, HPR and HY decreases with increase in VFA concentration (Lee et al., 2002).

3.7. Partial pressure

The partial pressure is increased due to the accumulation of hydrogen inside the reactor. The accumulation of hydrogen leads to the inhibition of forward reaction in reactor according to Le Chateliers Principle and thereby the HPP reduces the hydrogen production in reactor. The extraction of generated hydrogen from the system helps to overcome the impact of increase in partial pressure due to the accumulated hydrogen inside the reactor. The maintenance in partial pressure enhances the production of hydrogen (Junghare et al., 2012) and the introduction of nitrogen gas helps to extract the hydrogen gas by 68% (Mizuno et al., 2000).

3.8. Wastewater as a substrate for fermentation

Organic rich wastewater can be used as a substrate for efficient biohydrogen production since it reduces the overall treatment cost (Sivagurunathan et al., 2017; Laurinavichene et al., 2012). Industrial wastewater contains higher degradable organic matters which maintain the balance between the energy applied and recovered (Angenent et al., 2004). The research have been undergone by using the wastewater from cattle (Tang et al., 2008),sugar industry (Jayabalan et al., 2018; Lai et al., 2014), food processing industry, paper mill (Lakshmidevi and Muthukumar, 2010), rice winery, distillery (Wicher et al., 2013), chemical (Venkata Mohan et al., 2007a, 2007b), starch, palm oil mill, beverage(Kumar et al., 2015), cheese whey (Azbar et al., 2009), pharmaceutical (Krishna et al., 2013) as a substrate for the fermentation process. The increase in biodiesel production leads to excessive discharge of glycerol and it can be effectively used as substrate for biohydrogen production (Mahapatra et al., 2013; Sabourin-Provost and Hallenbeck, 2009; Rossi et al., 2012). Brewery wastewater along with enriched mixed culture at 5.5pH, 38.3 °C temperature and 16.6 g/l OLR gives the higher hydrogen production and shows that the substrate concentrations have a huge effect on the product (Sivagurunathan and Lin, 2019). Sivagurunathan et al. (2015) investigated the high fermentation rate of beverage industry wastewater in immobilized cell reactor and found that the HPR was 55 L/L-d with 1.5 h HRT and 320 g/L-d hexose equivalent OLR. They showed that the HPR value is higher than all other industrial wastewater fermentative hydrogen production. In a study by Cappelletti et al. (2011) cassava processing wastewater was used as a substrate and *Clostridium acetobutylicum* ATCC 824 as inoculum for the biohydrogen production. The increase in substrate concentration leads to the lower yield of hydrogen and substrate conversion efficiency. The lower concentration of COD increased the yield by 2.41 mol H_2/mol glucose and the result shows the efficient utilization of substrate for biohydrogen production. Lin et al., 2017 used textile desizing water (TDW) using coagulation pretreatment to produce fermentative biohydrogen. The result shows that the substrate concentration of 15 g total sugar/l reduces the hydrogen production using coagulation pretreatment and it indicate that the coagulation pretreatment at high concentration reduces the high content of toxic compounds which inhibits the hydrogen producing microorganisms. The hydrogen production ability increased to 120% and it shows the effectiveness of coagulation pretreatment. The coagulation pretreated TDW at the concentration of 15 g total sugar/l gave the HY of 1.52 mol/mol hexose and the HPR of 3.9 l/l-d. Kothari et al. (2016) investigated the production of hydrogen and methane using dairy effluent. The HY was 105 H_2 ml/g COD at 13 h HRT with 75% substrate concentration and the methane yield was 190 CH_4 ml/g COD. The economic analysis shows that the hydrogen energy have 0.22$/$m^3$ effluent benefit whereas methane production gives 0.336$/$m^3$ effluent. They concluded that the selected pathway of treatment selected gives efficient production of bioenergy. Table 1 represents the comparison of different wastewater used from industries for biohydrogen production.

3.9. Reactor configuration for biohydrogen production

Bioreactor configuration is the main impacting parameter that affects the biohydrogen production. Batch reactors are widely used in lab scale studies whereas in commercial scale, continuous stirred tank reactor (CSTR) has been widely used. Various types of reactors have been used for the production of biological hydrogen from industrial wastewater such as CSTR, Up flow Anaerobic Sludge Blanket Reactor (UASBR), Anaerobic Fluidized Bed Reactor (AFBR), membrane bioreactors and Packed bed reactor (PBR).

3.9.1. Continuous stirred tank reactor

CSTR can be used widely for continuous production of hydrogen and microorganism in which liquid can mix constantly due to the constant regime of mixing pattern. It facilitates higher contact between the substrate and the microorganism and thus obtains higher mass transfer. Due to the mixing pattern the CSTR is unable to hold large amount of microbes responsible for fermentation and thus the washout of microbes takes place at low HRT (Show et al., 2011). The reactor with mixed culture favours lower Solid Retention Time (SRT) for biohydrogen production since the methanogens are reduced (Waligorska, 2012). In order to overcome these limitations (biomass washout) cell immobilization is the possible option (Ding et al., 2016). The authors studied about CSTR treated yeast industry wastewater where the yeast cells were immobilized in polyvinylidene fluoride (PVDF) membrane. This reduces the biomass washout and favours higher hydrogen production. In addition, the authors have reported that the change in HRT and OLR had a great impact on the hydrogen production. The highest production was observed at 8 h HRT and OLR of 24 kg COD/m^3/d. They concluded that the efficient way to recover hydrogen is done by the restriction of methanogenic process by lowering HRT and OLR. Li and Li (2019) underwent a study using molasses wastewater for the integrated production of hydrogen and methane using CSTR-IC reactor. The volumetric HPR was 2.41 L/Ld at 30 kg COD/m^3/d OLR and the further increment in OLR decreases the production rate due to insufficient time for hydrolysis in CSTR.

3.9.2. Anaerobic Fluidized Bed Reactor (AFBR)

It shows the combinative action of PBR and CSTR. It has an excellent stirring capacity and low shear as compared to PBR and CSTR and it obtains an efficient mass transfer characteristics. The cells are attached as biofilms and the upward flow of wastewater maintain the biomass in suspension, thereby the catalytic activity increases which results in higher degradation of organics in wastewater. In AFBR the induced flow of liquid helps to enhance the fermentative hydrogen production with negligible substrate inhibition. It helps in the removal of gas produced, constant mixing of solid or liquid and reduces the pressure fall (Anjana et al., 2016). The biomass washout will be less in AFBR and it is considered to be more efficient. It can have the ability to work both at lower HRT and higher loading rate (Zhang et al., 2008).The energy required for fluidization is the only disadvantage of AFBR (Zhang et al., 2007). Amorim et al. (2014) studied the effect of propionic acid, OLR and HRT on HPR of cassava wastewater. With the increase in OLR and decrease in HRT, HPR increases. The hydrogen content in biogas increase with decrease in HRT to 2 h with OLR at 126 kg COD/m^3/d. VFA accumulation is also an important factor which affects the biohydrogen production as discussed in previous Section 3.6. Amorim et al. (2014) have suggested that the propionic acid accumulation happens at 8 h HRT which subsequently decrease the hydrogen production. They concluded that by decreasing the HRT to 1 h decreases the propionic acid accumulation and favours HY. Silva et al. (2019) used dairy wastewater as a substrate in AFBR for the efficient production of biohydrogen. They reported that immobilizing the biomass culture within the reactor enhances the HY. The maximum hydrogen production of 2.56 mol H_2 mol/carbohydrate was observed at 8 h HRT.

3.9.3. *Up flow Anaerobic Sludge Blanket Reactor (UASBR)*

In this type of bioreactors, the structure of granule and its enrichment leads to increase in hydrogen production. It consists of self-agglomerated granular microbial diversity and has higher capability of degradation, since the HRT is less (Banu et al., 2015). The blanket of granulated sludge is suspended in the reactor during operation and it can treat high organic strength wastewater rich in microbial population. Intanoo et al. (2015) used two stage UASB reactors to produce methane and hydrogen in mesophillic temperature. The first reactor was operated at 37 °C with pH control for hydrogen production and second reactor operated without pH control for methane production. The loading rate increased from 10 to 25 kg/m^3 d in first reactor. The maximum chemical oxygen demand (COD) removal was obtained at the loading rate of 25 kg/m^3 d and produced about 36.4% of hydrogen and 63.6% of carbon dioxide with no methane, since the methanogens got washed out. The methane production was about 83% at the loading rate of 8 kg/m^{3}d. They concluded that the two stage system increases the methane production rate as compared to single one. Krishnan et al. (2016) studied the effect of OLR in two stage UASBR-CSTR units under thermophilic condition in palm oil mill effluent (POME). The methane content decrease as the OLR increases and HRT decreases. At the loading rate of 75 kg/m^{3}d, the obtained hydrogen content was about 35%. In the same study, the VFA increased with increase in OLR from 25 to 100 kg/m^{3}d and it moderately increased beyond 100 kg/m^{3}d. The CH_4 content in CSTR increases with increase in OLR from 4 to 12 kg COD/m^{3}d and beyond that it decreases. The maximum methane content at 12 kg COD/m^3 d is 65%. The maximum VFA in CSTR was observed at 20 kg COD/m^{3}d. Overall COD removal of 85% was obtained in this study. They further concluded that the two stage reactor were efficient to generate methane and hydrogen from POME.

3.9.4. *Membrane bioreactor (MBR)*

It integrates the semi permeable membrane with the biological process and it is the combination of micro or ultra filtration with suspended growth bioreactor. It consolidates the features of membrane filtration and activated sludge treatment used for retention of microorganisms inside the reactor and the parameters such as HRT and SRT can be controlled (Oh et al., 2004). The increase in SRT increases the retention of biomass and thus increases the substrate utilization rate by decreasing the production of hydrogen. A study by Li and Fang (2007) shows the hydrogen production of 0.25–0.69 L/L h by using MBR. Buitrón et al. (2019) showed the feasibility of using granular sludge membrane reactor for biohydrogen production from brewery waste as inoculum. The increase in OLR decreases the HPR and HY in the reactor and the maximum HPR was obtained at the loading rate of 30 g/L/d. The increase in OLR to 60 g/L/d leads to decrease in hydrogen production due to metabolic shift to solvent production. The optimum production rate was achieved at 4 h HRT and determined that the resistance of membrane was controlled by solutes. The fouling of membrane is affected by formation of Extracellular polymeric substance (EPS) and operational flux.

3.9.5. *Packed bed reactor (PBR)*

These types of reactors are used for the conversion of biomass with high organic content. The can work efficiently at lower HRT without any extraction of biomass, where the beds of the reactor have a granule or biofilms (Show et al., 2011). The substrates are passed through column packed with biocatalyst. The performances of reactor for immobilized cells are based on the kind of immobilization. It advantages being its simple operation, anaerobic environment maintained by purging nitrogen and the elevated rates of reactions were possible through its operation. Perna et al. (2013) demonstrated a work on hydrogen production from cheese whey using Anaerobic Packed Bed Reactor (APBR) with different OLR. There is no much increment in yield as compared to other reactor configuration whereas the production was stable related to higher loads and the operational problem was negligible in this reactor. Palazzi et al. (2000) used continuous packed column for dark fermentation of starch by *Enterobacter aerogenes*. The bacteria are immobilized on fragments of spongy structures so as to reduce a stress on organisms while stirring and to limit the removal of microbial biomass from the reactor. The highest HY was 3.02 mmol H_2/mmol glucose.

4. Limitations and challenges of biohydrogen production

Despite of the remarkable merits the major limitation faced in biohydrogen production is limited substrate conversion potential and remaining fractions of substrate (wastewater) exist in acidogenic effluent during acidification process (Venkata Mohan, 2010). The prolonged buildup of acidogenic metabolites leads to decrease in pH. This in turn causes inhibition of hydrogen producing microbes and HY. These metabolites can enter the cell membrane of hydrogen producers and penetrate into the cell causing growth discrepancy, augments the ionic strength and cause cell cleavage. Therefore, energy maintenance is needed to retain the biological balance in the biomass. This minimizes the energy needed for biomass growth. The productivity of hydrogen is reduced when more metabolic by products such as lactic acids, ethanol, and propionic acid were accumulated as these compounds surpass the productivity of hydrogen. Integration of fermentation process with other approaches is the viable option to overcome the other metabolites. Another major limitation in continuous biohydrogen reactor is the biomass wash out. In order to overcome this limitation, immobilizing the biomass in support material and granulation in reactors is the promising choice. Another major challenge associated with biohydrogen production is the competition of methanogens over hydrogen producers. Selective enrichment and bioaugmentation are the emerging strategies to overcome the suppressive growth of hydrogen producing microbes. The emerging strategies such as immobilization, process integration, bioaugmentation and genetic engineering techniques have been discussed in detail in the forthcoming section.

5. Advancement and way forward to commercial application

Hydrogen production by microorganisms gained more attention for few decades due to the pollution less nature, recyclability and high efficiency of conversion of substrate. Microorganisms such as cyanobacteria, algae and bacteria were widely used for the efficient production of hydrogen from organic waste substrates (Gupta et al., 2013). The development of hydrogen production technologies are not widely accepted commercially due to its high cost of production and lower

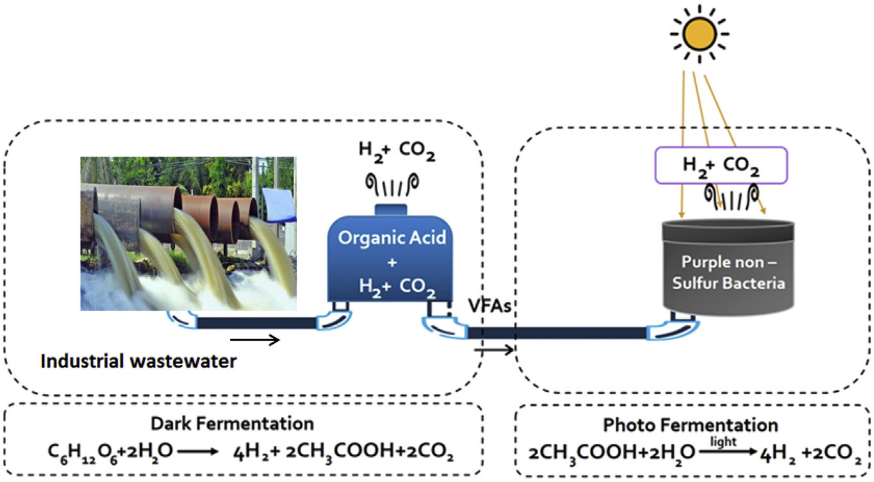

Fig. 1. Schematic representation of integrated process of biohydrogen production.

yield of hydrogen. The major challenges which prevent the commercialization of hydrogen production process are the selection of microorganism for hydrogen production, optimization of operational factors and design of reactors. The lack of storage of hydrogen, fuel cell technologies and distribution networks are the major barrier in technological means along with the pretreatment technologies and cost of hydrogen production are needed to be addressed for the production in commercial scale (Zhu and Lin, 2016).

Advancement in improving the hydrogen production are focused widely in recent years by introducing new production technologies such as bioaugmentation (Marone et al., 2012), cell immobilization (Kumar et al., 2016a, 2016b, 2016c, 2016d), integration of process (Chandrasekar et al., 2015), microbial electrolysis cell (Kadier et al., 2016) for improving efficiency and by incorporating genetic engineering (Srirangan et al., 2011). The basic improvement can be achieved by the cheaper substrate with pretreatment, high yielding strain and cost efficient reactors. The pretreatment of the substrates enriches the acidogenic bacteria by inhibiting the growth of methanogenic bacteria (Kumar et al., 2016a, 2016b, 2016c, 2016d; Kumar et al., 2017). The mild acid and microwave pre-treated corn stalk can provide the HY of 1.53 mol H_2/mol glucose at thermophilic temperature (Liu and Cheng, 2010). The study on economic viability and reusability were needed to carry out the integrated pretreatments for industrial effluents.

Immobilization is one of the techniques where the biomass attached to inert or supporting material and this material helps the biomass to remain in the reactor (for instance, CSTR). It is the promising technique to retain the biomass within the reactor to increase the yield and productivity of biohydrogen (Lutpi et al., 2016). Various support material can be used to attach the cells of biomass and repeating cultivation of mixed culture helps in increasing the growth of microorganisms (Kumar et al., 2012). Lutpi et al. (2016) used granular activated carbon (GAC) as a support material to grow hydrogen producing microbes in repetitive cultivation and obtained about 48–50% of hydrogen content in total biogas. Another enhancement strategy to enhance the biohydrogen production is process integration which reduces the inhibition of biohydrogen stimulated by the accumulation of metabolites during fermentation process.

Presently the integration of dark and photo fermentation anaerobically have widely adopted in large scale since the energy retrieval is high and increases the efficiency of wastewater treatment (Mishra et al., 2016). The process integration can improve the performance and suppresses the issues caused by single process (Rai and Singh, 2016). Dark fermentation is the efficient concept for biohydrogen production as compared to other methods and the integration of other system with dark fermentation increases the energy recovery. The two stage biological processes provide an efficient generation of biohythane (mixture of biohydrogen and methane) which are commercially used as an energy storage material in Germany and as a fuels for vehicles in India (Tapia Venegas et al., 2015). The schematic representation of integrated process of biohydrogen production is shown in Fig. 1. The manipulation in genes involves the insertion of desirable gene in the microbial strain to make it as a potent inoculum for biohydrogen production (Pinchukova et al., 1979).

Some modelling approaches are necessary to optimize the parameters and to compute the issues related with biohydrogen process. The computational fluid dynamics (CFD) tools is helpful to analyse the issues which are predicted prior to the real operation in case of scaling up of the process. This tool offers a balanced approach for scaling up or design and optimisation of various strategies for CSTR operating in industrial scale (Ren et al., 2011). Xu et al. (2010) performed a hydrodynamic assessment using CFD for industrial scale hydrogen production in CSTR and optimised the reactor from lab scale to industrial scale. The CSTR of 17 l capacity of CSTR in lab scale to 14,000 l capacity of CSTR in industrial scale was modelled. The two dimension Eulerian – Eulerian model was used to demonstrate the flow behaviour of liquid and gaseous phase. They suggested that the velocity heterogeneity and stagnation zone must be optimised for industrial scale reactor and for hydrodynamic analysis the reactor structure must be optimised. The SWOT (strengths, weaknesses, opportunities, and threats) analysis is another method to evaluate the strength and weakness of the system operation for upgrading the process towards industrialisation (Babatunde and Adebisi, 2012). PEST (Political, Economic, Social and Technological factors) analysis is used for understanding the market growth or decline in organisation (Hsu and Lin, 2016). Hsu and Lin (2016) investigated the feasibility of commercialisation of hydrogen production in Taiwan by using ESCO model. This model assessed the rate of return and concluded that the government promotion through subsiding the installation for hydrogen production helps to gain the rate of return to the investor.

Few studies have been studied in pilot scale by using the wastewater as substrate for the production of hydrogen. The pilot scale studies give an idea about the difficulties during operations. In order to understand the conversion of process to an external validating research the realistic pilot scale study is necessary. In a study by Vatsala et al. (2008) the distillery effluent was used as a substrate for the co culture of Rhodopsuedomonas palustris P2, Citrobacter freundii 01 and *E. aerogenes* E10 with the capacity of 100,000 L. The yield of hydrogen was 2.76 mol H_2/mol glucose. Ren et al. (2006) studied the efficiency of biohydrogen production from molasses in continuous mode with pilot scale reactor. The reactor rums for about 200 days and obtained the HPR and yield of 5.57 m3 H_2/m^3 day and 26,013 mol $H_2/kg_{CODremoved}$ at the varying OLR from 35 to 55 kg $_{COD}$/m^3 day.

The technology based economic analysis is needed to compare the efficient production of hydrogen compared with fossil fuels. The scaling up of the production to industrial scale decides the suitability of processes adopted. Hydrogen production through microbial pathway shows an excellent area where the future needs can be fulfilled in sustainable way. The efficient and proper design of bioreactors and the selection of substrate of lower cost are essential for the fermentation of hydrogen which contributes towards the global renewable energy. The development of reactor configuration are still challenging in large scale production. The integration of dark and photo fermentation helps to resolve the problems on inhibition of substrate and also increases the yield of hydrogen. The fermentative hydrogen production is promising one to achieve sustainability and economic viability in commercial application for future generation.

6. Conclusion

This review presents a detailed report on recent challenges, updates and operational changes of various biohydrogen producing reactors. The optimizations of operating conditions are necessary to upgrade the production with economic viability. Limited substrate conversion and low productivity are the two main issues associated with biohydrogen production process. The recent developments in these technologies help to overcome limitations and guide towards large scale implementation and commercialisation of biohydrogen production. The pilot scale studies have been undergone with different technologies, whereas commercialisation is still a great challenge due to its higher installation cost.

Declaration of Competing Interest

Authors declare no conflict of interest.

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