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REVIEW ARTICLE

Chronological perspective on fermentative-hydrogen from hypothesis in early nineteenth century to recent developments: a review

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Abstract
The first hypothetical hydrogen (H_2) production from biological means was proposed in the early of nineteenth century. However, the biological H_2 production technology did not received much attention until the anticipation of H_2 production was practically reported through anaerobic digestion of cellulose using microbes present in the ruminant tract in 1930s. Later on, subsequent development on fermentative H_2 production has been reported by researchers employing advanced technologies to the fermentative systems. The present review is envisioned to provide a technological devolvement's towards fermentative H_2 production from the late nineteenth to the present twenty-first century. The major technological aspects associated with H_2 production through the fermentative process such as genetic engineering, nanomaterial implementations, immobilization techniques, and reactor configuration developments were highlighted in this review.

Keywords Hydrogen · Technological developements · Genetic engineering · Microbial immobilization · Nanoparticles

1 Introduction

Indiscriminate use of conventional hydrocarbon fossil fuels and its production not only exhausted the limited reserves but imparted as a causative factor for imbalanced earth's ecological system [1]. The development of new technologies for sustainable energy production from organic-rich waste appears to be a promising approach in recent decades, which could simultaneously resolve the need for renewable fuels and the burdens of waste management [2, 3]. Waste treatment and simultaneous biofuel (H_2, CH_4, C_2H_5OH, etc.) production have considered a promising approach to mitigate this adverse situation [4]. In this aspect, as an alternative energy carrier, H_2 could be the "fuel of the future" as it exhibits higher intrinsic combustion calorific value of 143 MJ.Kg^{-1} than any other hydrocarbons with environmental credentials [5, 6]. H_2 is widely used for the hydrogenation of edible oil and synthesis of ammonia, which has winding its wide range of industrial applications [7, 8]. To address accelerated environmental pollutants, the quest for an advanced and economic way to produce this carbon-free gaseous fuel, various approaches have been applied till yet [5, 9]. The H_2 production process is classified into two major categories: chemical-physical and biological [10, 11]. The chemical-physical processes of H_2 production are limited due to various substrate characteristics and energy-exhaustive process (as required specific temperature and pressure), while the biological processes overruled these limitations.

Biological means of H_2 production is considered a promising approach towards low-cost and environment-friendly fuel production with simultaneous treatment of organic wastes. The application of biological processes for H_2 production was initially described in the early nineteenth century. Over a period of time, various technological advancements

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have been devoted to H_2 production using various agro-industrial waste as sustaninable resource. The present article tends to summarize the major technological development in dark fermentative H_2 production with diverse applications of genetic engineering to nanotechnological perspective based on available bibliographic literature.

2 Historical background

It was in the early nineteenth century that the first hypothetical production of biological H_2 was postulated [12]. However, it was not until the 1930s, when Woodman and his co-researcher has first reported a clear insight into the production of H_2 from anaerobic digestion of cellulose in the ruminant tract [13]. Since than, intensive research on H_2 production is underway, and several novel approaches have been implemented to surpass drawbacks associated with them. Following sustainable development and minimization of organic waste through fermentative process, H_2 is produced as a by-product during the conversion of organic waste into small organic acids with the help of H_2-fermenting microbes [14].

The fermentative H_2 production from algae in the presence of glucose was reported in the year of 1942 [15]. Later on, it was observed that anaerobic growth of *Rhodospirillum rubrum* in the absence of light causes metabolism of pyruvate (a metabolite of glucose) into H_2 molecules anaerobically [16]. Thereafter, several efforts have been made to enhance the H_2 production efficiency using different perspectives of microbiology including co-culture of photosynthetic bacterial species and dark fermentative bacterial species [17]; optimization of physicochemical conditions [18, 19]; application of fermentative immobilized bacterium (*Rhodospirillum rubrum*) [20]; use of hydrogenases enzymes in H_2 metabolism [16, 21]; isolation of efficient H_2 producers from various sources [22]; and employing nanotechnological approach [23, 24]. Further developments include study on the involvement of metal ions on H_2, CH_4, and CO production during batch anaerobic sludge digestion [25]. Moreover, the development of a stable system for the conversion of solar energy into H_2 using photosynthetic microorganisms (micro-algae) was an important milestone towards microbe-based H_2 production [26]. The isolation of halophilic H_2-producing bacterium *Haloanaerobium fermentans* from pufferfish ovaries and successful application in H_2 production from different organic wastes opened a new window of opportunity towards the development of a range of bacteria that have the potential to produce H_2 [27, 28]. However, the major interest in H_2 production by biological means has been exceptionally grown from early of the twentieth century, both in terms of application of wide range of organic waste and advancement in applied technologies. Table 1 shows some major achievements towards the fermentative H_2 production.

The rapid socioeconomic development has enforced all nations to develop an alternative approach for biofuel from sustainable resouscres [45]. The global research on H_2 production from sustainable sources increased significantly over the last two decades (Fig. 1). It is worth noting that the number of biological H_2-oriented research articles by fermentative means has been published in the year 2000 gradually increased in a significant numbers (including review articles) till 2019. Statistics have shown that China is the one leading contributor in terms of research articles on H_2 production followed by the USA and India, (Fig. 2a). As, in the early days of new China, there were limited H_2-based industries, while up to the 1990s, it increases about 107.2 times than that of 1949 [46]. Besides, China's outlook for future H_2 has been proposed in a traditional feedstock growth segments and projected 60-million-ton demand by 2050 [47]. A comprehensive review on wide range of organic waste that have been used for treatment with simultaneous production of $H_{2,}$ the industrial waste is accounted for almost 70% (Fig. 2b). It was possibly due to growing concern over industrial effluents which negatively affecting the environmental ecosystems, but at the same, it provides an economic and viable substrate for bioenergy.

This analysis of the historical data and energy technologies proves how fermentative H_2 production processes have been developed for the last 4 to 5 decades. The technological development of fermentative process for H_2 production has been rapidly evolving since then. These technical advances have been referred by the International Association for Hydrogen Energy [48]. The technological advancement in the fermentative H_2 production that has globally received significant consideration is particularly included genetic engineering, nanomaterial applications, immobilization technique, and bioreactor configuration.

This review summarizes the technological developments in fermentative H_2 production. So far, the focus has given to the fundamental technological advancement used for improved H_2 productivity. These approaches included genetic manipulation followed by nanotechnology. Further, the microbial immobilization technology used for H_2 production is being reviewed. Later, the development in reactor configuration towards improved H_2 productivity is discussed in this review.

3 Strategies for improving fermentative H_2 production

3.1 Genetic engineering for enhanced fermentative H_2 production

Redirection of the microbial metabolic process by limiting the production of the undesirable microbial product at the genetic level is an emerging approach to improve H_2 productivity [49,

Table 1 Milestones in fermentative H_2 production.

Time frame	Major milestones	Ref.
Early 1900s	Basic research established that algae and bacteria could produce H_2	[12, 29]
1931	In artificial media seeded with cultures of the bacteria has demonstrated the existence of two distinct anaerobic cellulose-fermenting organisms	[29, 30]
1942	Fermentative photochemical production of H_2 in algae	[15]
1977	Fermentative metabolism of pyruvate by *Rhodospirillum rubrum* after anaerobic growth in darkness for H_2 production.	[16]
1984	Photoproduction of H_2 from glucose by a co-culture of a photosynthetic bacterium and *Clostridium butyricum*	[17]
1984	System determination for the carbon flow from biopolymers to biogas by syntrophic interactions of acetogenic bacteria with methanogens at the level of interspecies H_2 transfer	[31]
1984	Optimization criteria for the stabilization of sewage sludge and biogas production through anaerobic digestion	[20]
1985	Cells of *Rhodospirillum rubrum* have been immobilized in various gels and tested for photobiological H_2 production	[32]
1986	Active participation of Hydrogenase enzyme been reported in Chlorella (an algal sp.) which favors anaerobiosis	[21]
1987	Fermentative H_2 production from new bacterial strain of *Enterobacter aerogenes* E. 82005	[33]
1987	H_2 production potential of fermentative microorganisms isolated from nepheloid layer of Sargaaso sea.	[34]
1987	H_2-production from glucose using anaerobic rumen fungus *Neocallimastix frontalis*	[19]
1987	Effective of various external factors on fermentative H_2 production using *Clostridium butyricum* strain NCTC7423 is investigated	[35]
1989	The effect of metal oxides on methane production and H_2 and carbon monoxide levels during batch anaerobic sludge digestion	[25]
1995	H_2 production by photosynthetic microorganisms	[26]
1998	H_2 production using co-culture of strict and facultative anaerobes from starch	[22]
1998	H_2 production from starch by a mixed culture of *Clostridium butyricum* and *Rhodobacter* sp. from starch	[36]
2000	Halophilic H_2-producing bacterium *Haloanaerobium fermentans* isolated from pufferfish ovaries	[27]
2000	Successful investigation of H_2 production various organic wastes	[37]
2002	Characterization of a H_2 producer from granular sludge	[38]
2007	Microbial H_2 production with *Bacillus coagulans* IIT-BT S1 isolated from anaerobic sewage sludge	[39]
2007	Assessing optimal fermentation type for H_2 production in continuous-flow acidogenic reactors	[40]
2013	H_2 production from industrial wastewater using immobilized mixed culture	[41]
2007	H_2 production from glucose by metabolically engineered *Escherichia coli*	[42]
2011	Bioreactor design for continuous dark fermentative H_2 production	[43]
2016	Two stage sequential dark and photo fermentation of industrial wastewater	[44]
2018	Nano-metal application for H_2 production in anaerobic digestion of industrial wastewater	[23]

50]. The metabolic engineering approach provides enhanced H_2 productivity by switching off or by alteration in particular genes that limit the H_2 production [51]. Nath and Das (2004) summarized the possible genetic engineering approach to improve H_2 production which includes (a) overexpression of H_2 evolving hydrogenases, (b) elimination of uptake hydrogenases, and (c) overexpression of cellulases, hemicellulases, and ligninases enzymes that help to maintain substrate availability [52]. Two well-characterized metabolic pathways for H_2 production are the formate pathway and nicotinamide adenine dinucleotide (NADH) pathway. Both pathways have been independently investigated by researchers and reported the existence of a linear relationship between the H_2 yield with the relative change in NADH pathways [53]. Formate metabolic pathways are catalyzed by pyruvate formate lyase (PFL) and formate hydrogen lyase (FHL) enzyme complexes. The FHL enzyme complex is the core enzyme of formate pathway that further comprises of formate dehydrogenase (FDH) and hydrogenase. Most of the genetic manipulations have been performed on FHL-related genes to regulate the formate

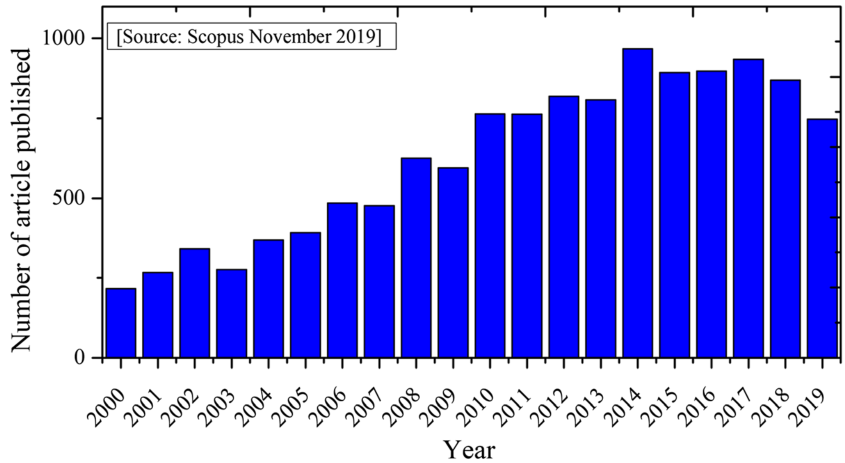

Fig. 1 The number of articles on biohydrogen. These data based on the number of articles mentioning biohydorgn in the citation database Scopus in November 2019

pathway and increase the production of H_2, as observed in Fig. 3 [54, 55].

The successful increased H_2 production through in vivo genetic engineered modes using *E. coli* strains have been investigated by several researchers and comprehensively reviewed by Maeda and his co-authors [51]. Such metabolic modification included the over-expression of particular genes such as cellulases, hemicellulases, and ligninases which increases the complex carbohydrate consuming ability of microbial strains and resulted in increased H_2 productivity [56]. Research on targeted regulation of NADH-based metabolic pathways to increase H_2 production also has been reported [57]. The reduction of ferredoxin with NADH using reverse electron flow has been anticipated to produce enough reducing power to enhance H_2 production by hydrogenases [58]. The major fermentative microorganisms used in the dark fermentation system are *E. coli* [59], *Clostridium* sp. [44], *Enterobacter* sp.[60], and *Bacillus* sp. [61]. Applications of *E. coli* and its genetically modified strains were reported for the capability to use maltodextrins as carbon sources plus oversecretion of endogenous alpha amylase [62]. Another attempt of mutant *E. coli*, HD701, has been reported for unregulated hydrogenase strain that has engineered to metabolize sucrose as feedstocks for H_2 production as an alternative to coupling-in and upstream invertase [63]. In a study, mutant *E. coli* with deleted uptake hydrogenase ▵*hyaAB* and ▵*hybABC* has reported an increase in H_2 yield by 10% over the wild-type strain of BW25113 from glucose. The deletion of lactate dehydrogenase (IdhA) and fumarate reductase (frdBC) increases the H_2 yield by 22 and 23%, respectively, in the mixed-acid fermentation pathways [64]. When the *Clostridium* species were fostered by disabling the uptake of hydrogenases enzyme, it has been reported for more robust H_2 production incompared to the wild one [65]. The transcriptomic and proteomic analysis of *Clostridium butyricam* CWBI1009 was studied by Calussinska et al. where they have provided a bio-molecular overview of the changes that occur during the metabolism shift of H_2

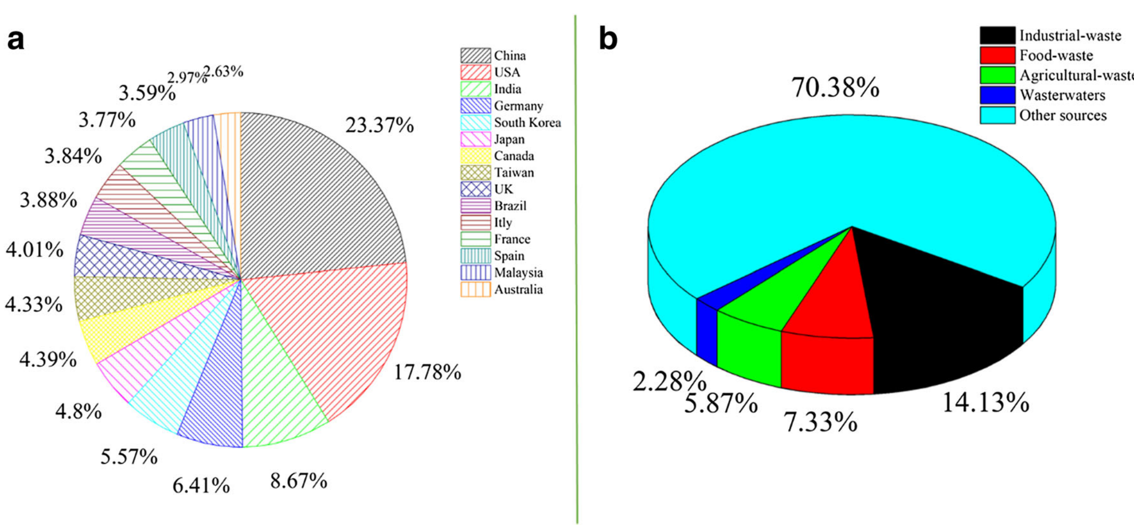

Fig. 2 Biohydrogen in citation database Scopus in November 2019. **a** country-wise sharing of articles based on biohydrogen. **b** Substrate applied for fermentative H_2 production and reported in research publications

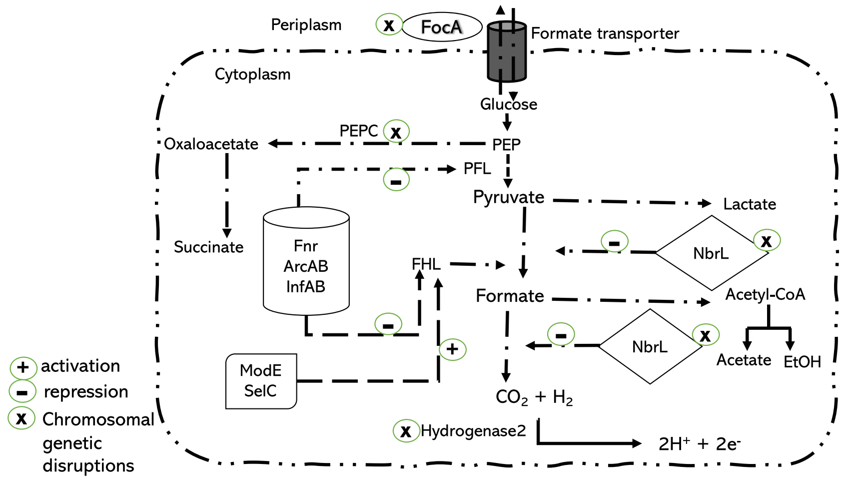

Fig. 3 H_2 production oriented metabolic pathways and genetic enegineering apparoches in *E. coli*, Adapted from [29]. *PEP* phosphoenol pyruvate, *PFL* pyruvate formate lyase, *FHL* formate hydrogen lyase, *LDH* lactate dehydrogenase

production [66]. Metabolically engineered mutant with an inactivated ack gene, which encodes acetate kinase in *Clostridium* sp. for the inhibition of acetate pathways, was investigated to improve H_2 production. Study reported 50% of more H_2 by mutant *Clostridium* sp. than the wild type of strain from glucose [67]. Besides, developing a O_2 tolerant H_2 producing strain and selectively inactivating the genes to prevent O_2 interference with this enzyme's activity also have been reported for increased H_2 production [68, 69]. *Thermococcus onnurineus* NA1, a genetically modified FrhAGB encoding gene is reported increased H_2 produced by increasing its O_2 tolerance activity. This strain was able to overcome the inhibitory effects of O_2 and demonstrated increased microbial growth and H_2 production under oxic conditions [70]. Further, approach to improve H_2 production has been reported by altering microbial genes which compete or interferes with the H_2 producing metabolic pathways [71]. The genetic manipulation efforts have accelerated the understanding of the H_2 research area by providing a deep insight into complex interactions taking place between the various metabolic pathways and hydrogenase enzymes. Evidently, the genetic manipulation of H_2-producing microbes seems an effective approach for improved H_2 production. It is anticipated that the genetic manipulation will not only help to improve H_2 productivity but also it can help to predict a pattern for H_2 producers and which will provide new insight on metabolic alteration. In addition, the data mining of microbial genomic and metagenomic sequences could also lead the researchers to revolutionize H_2 industries near the future.

3.2 Nanotechnology-based approaches for enhanced fermentative H_2 production

The unique physical and chemical properties of NPs are well known for its improved biocatalytic activities in fermentative system [72]. The additive of nano-scaled macro- and micronutrients to the fermentative medium has gained a new direction to heighten H_2 productivity by accelerating the microbial bioactivity in different pathways as depicted in Fig. 4 [73]. Hydrogenase and Nitrogenase are considered as key enzymes which are responsible for the microbial H_2 production [74] and the presence of metal ions (e.g., Ni, Fe) at its active get influenced by additive NPs to the culture medium [23, 75].

Over the last few years, several studies have been reported for advanced nanometals and their oxides and investigated its applications for the advancement of fermentative H_2 production [5, 76–78]. The remarkable assortment of novel structure and exceptional catalytic activity of nanoscale materials has been investigated by several researchers to increase the production of H_2 through fermentative process [79]. Among the abundance of nanoscale materials, Ag-oxides [80], Au-oxides [81], CuO_2, Fe, Fe_2O_3, Fe_3O_4, Ni, NiO, CoO [75], Pd-oxides, SiO_2, carbon nanotubes, and TiO_2 have been investigated and used as the catalyst for fermentative H_2 production. Zhang and Shen have investigated (for the first time as claimed by the authors) the application of gold oxide nanoparticles and concluded that the addition of 5-nm gold nanoparticles resulted in 46% higher H_2 productivity from artificial wastewater [82]. The improvement in the yield was explained by the hypothesis that the gold nanoparticles acted as electron-sink due to their higher affinity for electrons, which facilitated the further reduction of protons to molecular H_2 in the fermentative medium.

The NPs also behave as an antimicrobial agents as it can easily penetrates the cell membrane and causes cell lysis [83]. Therefore, the immobilization of nanoparticles showed a positive impact on microbial H_2 production. A significant increase in H_2 yield has been reported by the addition of nanoparticle of Pd, Ag, Cu, and Fe oxides immobilized in a porous matrix of silica [84]. Taherdanak et al. [63] investigated the effect of zero-valent Fe and Ni compared with Fe^{2+} and Ni^{2+} nanoparticles (in the range of 0–50 mg/L) on H_2 production

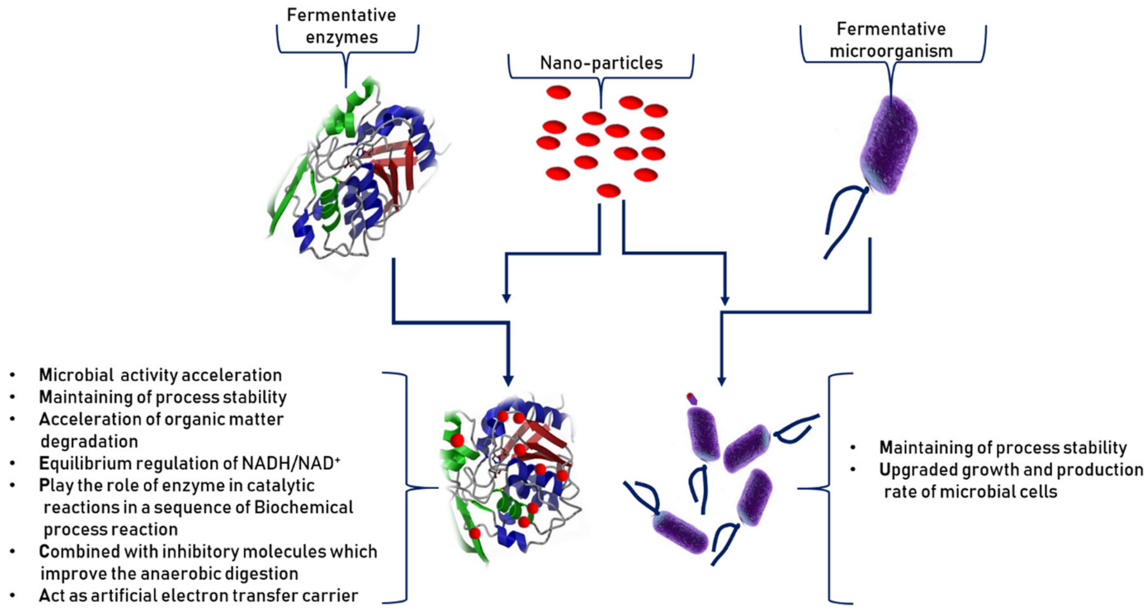

Fig. 4 Schematic representation of possible strategies to couple nanoparticles to key enzymes participate in the metabolic process or H_2-producing microbes for improved H_2 production

using glucose as carbon source and heat-shocked anaerobic sludge as inoculum. The results demonstrated a significant increase in H_2 yield of 55 and 15%, while the fermentative medium was supplemented with Ni^{2+} and Fe^{2+} nanoparticles, respectively [85]. Moreover, the addition of NiO_2 and CoO_2 nanoparticles to the substrate have reported substantial increase in H_2 production by 1.51- and 1.61-fold, respectively [75]. Zho et al. [58] reported a 67.6% increase in the H_2 yield using 20 nM Ag-oxide nanoparticles in the medium using glucose as the carbon source and *C. butyricum* dominated mixed culture as inoculum. Taherdanak et al.[63] described the comparative impact of Fe ions and Fe^{2+} nanoparticles as supplements (0–50 mg/L) in the fermentative medium containing glucose as substrate and anaerobic sludge as inoculum. A 37% increase in H_2 yield was reported with the addition of 52 mg/L of Fe^{2+} nanoparticles [85]. In addition to these, several nanoparticles of metal ions and oxides have been studied by using different carbon sources and a profound effect on H_2 yield enhancement was observes as presented in Table 2.

These nanoparticles mostly increase the H_2 production through their substantially effects on the microbial growth, substrate conversion efficiency, and microbial metabolic profile (Fig. 4). It is believed that in the presence of nanoparticles, H_2 producer shifts intermediate metabolites towards the higher production of organic acids including acetate and butyrate and reduces the production of alcohol (an inhibitor to H_2 production) [52]. However, the uncertainties on optimal concentrations of nanoparticles are still in the quest as the minimal toxicity of nanoparticle on fermentative microbes is of prime requirement. The metalloenzymes need optimal dosages to balance their catalytic activities as well as prevents feedback inhibitions [77]. Further, the identification of novel nanoparticle with significant physicochemical properties from economic sources and their impact on H_2 production need to be explored for improved H_2 production.

3.3 Immobilization for enhanced fermentative hydrogen production

Immobilization technologies are in existence for many decades and suceesfully applied in various sectors including wastewater treatment, pharmaceuticals, and food industries [92]. The immobilized culture has distinguished property as they cannot move independently in aqueous media which helps to maintain enough biomass concentration in the fermentative medium [11]. The matrices used for microbial immobilization which are inert nature assist in the adsorption of specific nutrients from organic waste during fermentative H_2 production [93]. The immobilization can catagorized as entrapment in polymers, confinement in the liquid-liquid emulsion, affinity immobilization, adsorption and covalent coupling [94]. These immobilizations further grouped as “active” (chemical attachment, flocculant agents, and gel encapsulation) and “passive” immobilization (by using microbial natural tendency to attach with the surfaces-natural or synthetic and grow on them) [95]. The schematic representation of the immobilization techniques is illustrated in Fig. 5. Various cell immobilization processes have been adopted to improve H_2 productiviton in a continuous system, including biomass immobilization, adsorption to the solid surface, biofilms, granules, and entrapment in polymeric gels. The entrapment of fermentative inoculum within the carrier matrix is a widely used system

Table 2 Nanoparticles mediated microbial H_2 production

Nanoparticles	Substrate	Inoculum	Temp.	Initial pH	NPs	H_2 yield (mol/mol-hexose)	Ref.
Hematite NPs	Sucrose	*Clostridium* sp.	35 °C	8.48–6.00	200 mg/L	3.21 3.57	[86]
Pd-oxide NPs	Glucose	*Enterobacter* *Cloacae* dominated mixed culture	37 °C	7.00	5.0 mg/L	1.48 ± 0.04 2.48 ± 0.09	[87]
Ag-oxide NPs	Glucose	*Clostridium* sp. dominated mixed culture	35 °C	8.00–9.40	20 nmol/L	2.48	[80]
Cu-oxide NPs	Glucose	*Enterobacter* *Cloacae* and *Clostridium* sp.	37 °C	7.00 and 6.00	2.5–12.5 mg/L	Inhibitory effect	[88]
Ni-oxide NPs	Glucose	Anaerobic microbial flora	35 °C	5.61	5.67 mg/L	2.54	[89]
Iron oxide NPs	Molasse wastewater	Mixed bacterium consortium	37 °C	6.00	50 mg/L	[a]44.28 .	[90]
Magnetite NPs	Bagasse	Sludge (heat treated)	30 °C	5.00	200 mg/L	0.874	[91]

a: mL H_2/g COD

for providing an adequate anaerobic environment for microbial processes and to improve the H_2 productivity [93].

Recently, the fermentative H_2 production using immobilized inoculum have been reported in various studies, as it limits the fermentative medium contamination by unwanted microbes and it also helps to stabilize the inoculum proportions in the medium by preventing cell washout [96, 97]. As the H_2 production by using suspended culture is prone to washout during continuous mode, the immobilized culture maintains the culture stability and result improved H_2 productivity [98]. Singh et al. have reported the improved H_2 production of 380 mLH_2/g-COD consumed using *Clostridium butyricum* LS2 culture immobilized polyethylene glycol in continuous mode at hydraulic retention time (HRT) of 16 h [99]. In another study, threefold increase in H_2 production has been reported when the mixed microflora was immobilized in alginate beads supplemented with chitosan and titanium oxides [100]. The increase carbohydrate consumption of 88% with maximum H_2 yield of 2.1 mLH_2/mL-POME (palm oil mill effluent) has been reported by Ismail et al., when POME wastewater was fermented under a

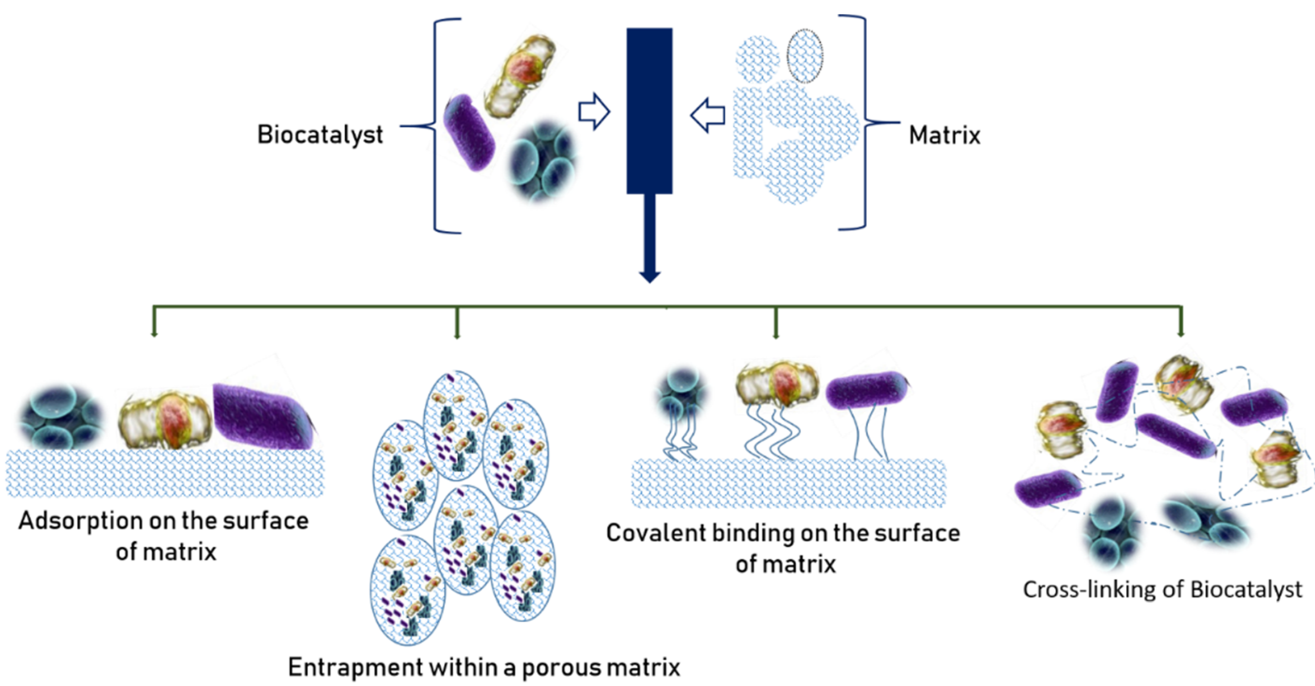

Fig. 5 Methods employed for microbial H_2 production. **a** Cell or enzyme immobilization by adsorption/attached to the surface of the matrix. **b** Immobilization through entrapment/microencapsulation of cell or enzyme in porous matrix. **c** Covalent binding of cell or enzyme to the nanoparticles. **d** Covalent cross-linking of cell or enzyme

continuous mode for H_2 production [101]. Acclimatized sludge immobilized into the composite polymeric matrix (polymethyl methacrylate/collagen/activated carbon) has reporte a significant increase in H_2 production from 1.21 $mLH_2/mL/h$ (suspended system) to 1.80 $mLH_2/mL/h$ (immobilized system) under relatively low organic loading rate (OLR) from synthetic wastewater [102]. Further, the improved H_2 production have reported by Zhao et al., when they performed a continuous mode of fermentation using *Clostridium sp.* T2 immobilized on mycelia pellets. The maximum H_2 production rate of 61 mL $H_2/L/h$ was reported at HRT of 10 h compared with the suspended one [103]. The number of researchers has been reported the effectiveness of immobilized microbial cells for the enhanced production of H_2 as depicted in Table 3.

The advantages associated with H_2 production using immobilized inoculum systems are well established which include reduced risk of microbial contamination, high cell density maintenance biocatalyst recycling, and increased rate of productivity. However, the reported matrices used for immobilization were synthetic polymers or inorganic materials which possess disposal problem and often toxic to microorganisms. Therefore, cheap, organic, non-toxic, and environmentally friendly matrices should be explored in near future to improve the H_2 production. Moreover, the development of genetically engineered tailored for immobilization and implementation of innovative strategies could be the progressive advancements towards the improved H_2 productivity.

3.4 Bioreactor configurations and fermentative H_2 prodution

Bioreactor configuration affects the microbial homogeneity, hydrodynamic activities, bioprocess activity, substrate accessibility to the microbes, microbial population, mode of operation, etc, [110]. However, every bioreactor exhibits its own benefits and drawbacks. The H_2 yield and substrate conversion rate by H_2 producers are highly influenced by the reactor type and its operating conditions [111]. Various researches have been investigated for H_2 production using the diverse range of bioreactor technologies and concluded that the H_2 productivity is not only dependent on bioreactor type but also dependent on the modification tailored for the particular purpose. The reactors tailored for H_2 production can be categorized into suspended and immobilized bioreactors. Continuous stirred tank reactor (CSTR), anaerobic membrane bioreactor (AnMBR), and anaerobic sequencing batch reactor (ASBR) are the suspended bioreactors, while upflow anaerobic sludge bioreactor (UASBr), anaerobic fluidized bed reactor (AFBR), and expanded granular sludge bed reactor (EGSBr) are immobilized bioreactors as shown in Fig. 6 [112]. The major advantages and disadvantages of different types of bioreactors for H_2 production are listed in Table 4. Generally, the most H_2 production experimentation process is accomplished in batch mode bioreactor for lab-scale purposes and continuous type bioreactor for industrial scale [96]. Besides, CSTR has been widely used for a long time fermentative H_2 production process both at the lab-scale as well as

Table 3 Immobilization of pure and mixed culture on the different matrix for fermentative H_2 production

Matrices/supportive	Feed	Reactor	Feed concentrations	Fermentative Inoculum	Temperature	Initial pH	Bio-H_2 Yield	Ref.
Calcium alginate	Cheese whey-	Batch mode (glass serum bottles)	10 g lactose/L	*Enterobacter aerogenes* MTCC 2822	30 °C	6.8	3.45 mol H_2/mol lactose	[104]
Polymethyl methacrylate	Sucrose-based synthetic wastewater	Continuous-flow reactor	20 g COD/L	Acid pre-treated acclimated sludge	35 °C	6	2.25 mol H_2/mol sucrose	[102]
Agar	Sodium formate	Batch mode (serum vial)	100 mM	*E. coli* SH5	37 °C	6.5	1 mol H_2/mol formate	[105]
Ethylene-vinyl acetate copolymer	Sucrose	Batch mode (serum vial)	20 g COD/L	Acid pre-treated anaerobic sludge	40 °C	6.7	1.41 mol H_2/mol sucrose	[106]
Polyethylene–octene–elastomer	Sucrose	Continuously stirred tank bioreactor	20 g COD/L	Acid pre-treated anaerobic sludge	35 °C	6	1.7 mol H_2/mol sucrose	[107]
Polyester fiber	Acid hydrolyzed wheat starch	Batch mode (glass serum bottles)	13 ± 1 g TS/L	Heat and acid pre-treated anaerobic sludge	55 °C	5.5–6	1.96 mol H_2/mol glucose	[108]
Metal mesh covered plastic scouring sponge pad	Acid hydrolyzed wheat starch	Batch mode (serum bottles)	10 g TS/L	Heat and acid pre-treated anaerobic sludge	37 °C	7	2.1 mol H_2/mol glucose	[109]

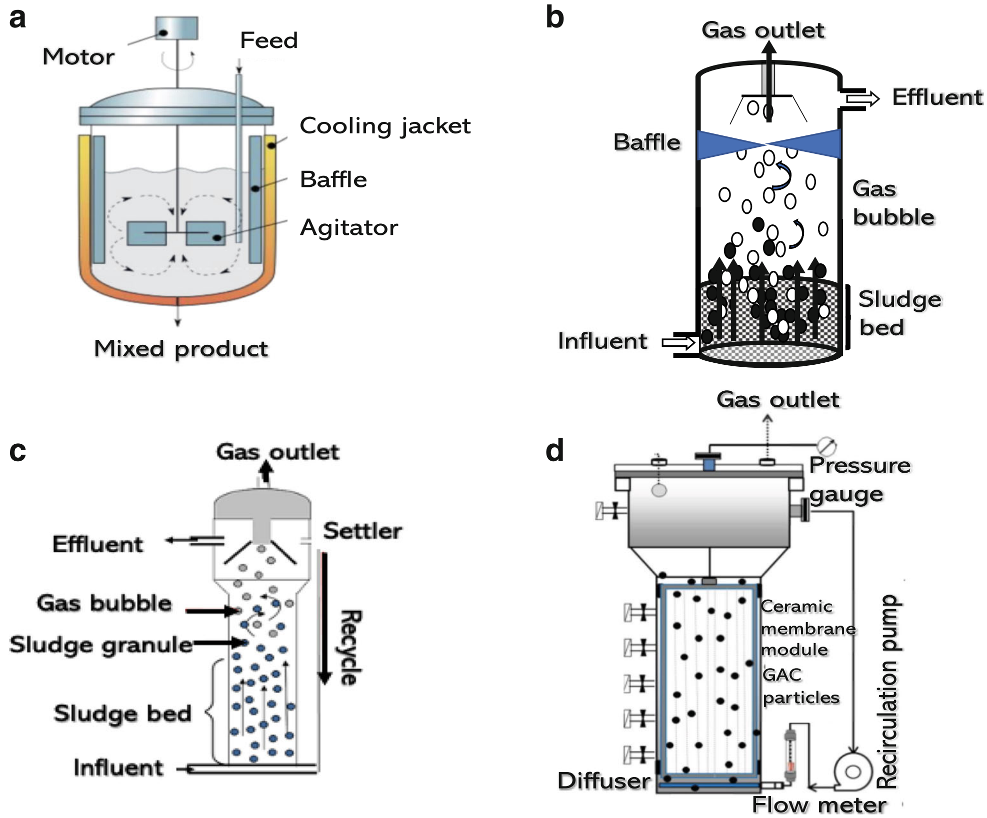

Fig. 6 Schematic representation of bioreactors for fermentative H_2 production. **a** Continuous stirred tank reactor. **b** Upflow anaerobic sludge blanket reactor. **c** Expanded granular sludge bed reactor. **d** Anaerobic membrane bioreactor [Adopted and modified from 117,118]

industrial scale. However, over the time the application of CSTR has declined due to its limitations of biomass washout and short retention time [113].

High sensitivity to the physical conditions (including temperature, pH, HRT) and poor biomass settling are the major constraints of CSTR, which limits it to large-scale production of H_2 in continuous mode [114]. Suspended cell bioreactors and CSTR are found to be mostly used bioreactors, while UASBr and AFBR have become popular for their higher H_2 production potential [110]. Various reactor designs have been evaluated to examine the continuous H_2 production using granular sludge in UASBr and CSTR. The higher production rate of H_2 during the continuous process in AFBR, CSTR, and UASBr is mainly correlated with the biomass concentration which influences the reactor performance [115]. CSTR has a relatively short retention period as compared with other

Table 4 Advantages and disadvantages of biorecaters used for fermentative H_2 production

Recator type	Advantages	Disadvantages
CSTR	○ Simplicity, and the ease of monitoring and controlling scale up. ○ Able to provide efficient gas transfer to cells ○ Mixing achieved by means of an impeller, as the impeller speed will be sufficiently high enough to ensure that each phase of the vessel contents is of uniform composition	○ Low biomass retention
APB	○ Good retention of biomass	○ Clogging ○ Lower mass transfer than FBR
GSBR	○ Hydraulic mixing regime is less turbulent comparing with the CSTR, this results in higher mass transfer resistance	○ Excessive shear stress can detach biomass ○ Energy required for FBR
UASB	○ Good treatment efficiency and capability in retaining high biomass concentration	○ Slow development of granules

**CSTR*continuous stirred tank reactor, *APB* anaerobic packed bioreactor, *GSBR* granular sludge bed reactor, *UASB* upflow anaerobic sludge bioreactor, *FBR* fluidized bed reactor

reactor types including UASBr because of the better mass transfer performance. However, it requires continuous supervision to prevent cell deposition and its washout at inadequate operating parameters. The washout problem has been troubleshot by performing the fermentative process using membrane bioreactor and by immobilizing the sludge or inoculum in suitable supporting materials (e.g., fixed-bed bioreactors) [96]. The application of UASBr is a promising approach for improved H_2 productivity and to treat high-strength organic wastewater. The granulated sludge applied in UASBr can retain maximum inoculum/microorganism, which helps in waste stabilization. In addition, efficient particle separation, high OLR, short HRT, and low set-up space requirement are the features of UASBr which make it an ideal reactor for harnessing H_2 by improved productivity. These alternatives demonstrated the process to be more robust and economic with enhanced H_2 productivity [111]. The advancement in reactor development would make a worthwhile contribution to overcome the limitations in H_2 production and to increase the potential of fermentative H_2 production from organic waste. Somehow, the knowledge of adequate configuration is still a prerequisite for optimum process conditions and performance. Recurring this will not only resolve the H_2 energy concern but also by economic and environmental means.

4 Conclusive remarks and future prospect

The extensive research on the technological development of fermentative processes in the past three decades has shown the promising improvement in H_2 productivity from different types of substrate. A technological breakthrough can be observed with the incorporation of genetic engineering, nanoscale technology, immobilization techniques, and advancement in rector configuration into fermentation technology. To improve the H_2, it is important to use highly efficient genetically engineered microorganisms such *Clostridium* sp. becomes promising trends. Considering the benefits of nanoparticles, various research has been demonstrated for improved H_2 productivity under controlled laboratory scale experimentations. Although, the nanoparticles exhibit microbial toxicity the optimum concentrations could drastically influence the H_2 productivity. Besides, the use of microbial immobilization for H_2 production have evidented beneficial as it increases operational stability, minimizes the contaminations, and extends the fermentation period which subsequently increases the H_2 productivity. The H_2 production effected by the configurations of bioreactors along with operating conditions. Although various configured reactors are known for H_2 production, CSTRs are the widely used bioreactors for H_2 production in continuous mode due to its relatively simple, ease of monitoring, and rapid start-up phase. The future research on cost-effective scaling up and broadening H_2 production on industrial level needs to be focused on the development of highly active genetically modified H_2 producer and new insights on immobilization techniques and matrix. The design and configuration of industrial scale H_2 production specialized reactor development is expected to be more effective for H_2 production.

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