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Review

Lignocellulose biohydrogen towards net zero emission: A review on recent developments

Chyi–How Lay, Jeyaprakash Dharmaraja, Sutha Shobana, Sundaram Arvindnarayan, Retnam Krishna Priya, Rajesh Banu J, Rijuta Saratlae, Young Kwon Park, Vinod Kumar, Gopalakrishnan Kumar

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1   **Lignocellulose biohydrogen towards net zero emission: A review on recent developments**

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Abstract

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32   This review mainly determines novel and advance physical, chemical, physico–chemical,

33 microbiological and nanotechnology–based pretreatment techniques in lignocellulosic biomass

34 pretreatment for bio–H2 production. Further, aim of this review is to gain the knowledge on the

35 lignocellulosic biomass pretreatment and its priority on the efficacy of bio–H2 and positive

36 findings. The influence of various pretreatment techniques on the structure of lignocellulosic

37 biomass have presented with the pros and cons, especially about the cellulose digestibility and

38 the interference by generation of inhibitory compounds in the bio–enzymatic technique as such

39 compounds is toxic. The result implies that the stepwise pretreatment technique only can ensure

40 eventually the lignocellulosic biomass materials fermentation to yield bio–H2. Though, the

41 mentioned pretreatment steps are still a challenge to procure cost–effective large–scale

42 conversion of lignocellulosic biomass into fermentable sugars along with low inhibitory

43 concentration.

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45 ***Keywords:*** *Lignocellulosic biomass; bio–H_2; Pretreatment; Nanotechnology; Challenges.*

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1.   Introduction

The lignocelluloses have been originated from both the edible and non–edible industries and are sustainable as well as promising materials for the productivity of second generation bio–fuels, which mainly include bio–ethanol, bio–H_2, biogas, bio–methane, synthetic bio–fuels, bio–diesel *etc*. Lignocellulosic biomass is a renewable resource and an interesting alternative for fossil fuels since it consists of large amounts of energy as well as organic compounds. Further, lignocelluloses are a basic components of plant materials and has widely been utilized by biorefinery, cosmetic, food and pharmaceutical industries, as well (Ashokkumar et al., 2022; Kumar et al., 2019; Ponnusamy et al., 2019). In the way, such materials obtained from flowers, energetic willow, grasses, miscanthus, poplar trees, and stems, are functioning as fillers in the fabrication of beauty masks, curative chows and thermoplastic composite materials. Some other significant sources of the lignocellulosic biomass materials are the residual forms procured from agricultural wastes, cereal, corn straw, corncob, forest, paper industry, potato haulms, rapeseed oil pressing, sawmills, sugar beets, sunflowers, waste paper industries and other waste fragments of plants as well as firewood (Azbar et al., 2009). The biomass structure only defines the kind of pretreatment techniques, required. The bio–H_2 that is procured from lignocelluloses *via* fermentation is an alternative to petro–derived fuel itself as it is eco– friendly since there is no emission of GHGs (greenhouse gases), mainly CO_2 (carbon dioxide) while its combustion (Moreno and Dufour, 2013). Further, bio–H_2 is a basic molecule in a range of chemicals as well as petro–chemical processes, like production of ammonia, integrated circuits and optical fibers, methanol, methane, nitrobenzene derived aniline from nitrobenzene, polymers syn–gas, hydrogenation derived olefins, *etc*. Bio–H_2 is also used in the petro–chemical processes of hydro–amination, hydro–cracking and hydro–conversion (Gómez et al., 2011). Beyond from the lignocellulosic bio–energy source, the bio–H_2 can crucially be generated with energetic potentiality by means of gasification from coal & coke, reforming process of steam methane as well as water gas from crude oil derived hydrocarbons, electrolysis of water and water gas shift. All such processes not only need a high input of electrical power and fossil fuels utilization but also depletion of green environment by means of air pollution. So, bio–resources have been considered for larger scale production of bio–H_2 (Goryunov et al., 2016). In such a way the biomasses can be an alternative option to produce sustainable bio–H_2 energy to achieve short–

93 term emission reductions (Balat, 2011). In the Europe, about 67% of preliminary energy has

94 been procured primarily from biomass renewable resources with nearly about 14–19 MJ/kg

95 calorific value and further the produced total bio–energy electricity is about 370 TWh, initially

96 from the year of 2012. According to IEA (International Energy Academy), it occupies absolutely

97 1.5% of the generation of world electricity (Sun and Cheng, 2002). The lingo–cellulosic

98 materials biorefinery yield nearly 48 % of the biomass–derived energy under favorable

99 circumstances (Sun and Cheng, 2002). The main by–products of bio–refineries apart from the

100 bio–H_2 are the biomaterials and certain bio–chemicals *viz*. bio–ethanol and furan are very

101 important for environmental energy security as it possesses socio–economic advantages

102 associated with biodiversity, food security, reduction of greenhouse gases emission, and

103 sustainable bio–energy development (Balat, 2011; Sun and Cheng, 2002). The generation of

104 energy/power forecasts that the produced energy has been raised from 200 TWh by the year of

105 2006 to 380 TWh by the year of 2016, globally and it has reached 600 TWh in 2020 (IEA, 2015).

106 The limitation of lignocellulosic derived bio–H_2 *via* fermentation is the formation sugar

107 intermediates during hydrolysis. Thereby, it requires a proper lignocellulosic pretreatment in

108 bio–H_2 productivity. The aim of the pretreatment technique includes change in the rigid

109 lignocellulosic by means of digestion to increase the accessibility of a range of hydrolytic

110 reagents/factors like suitable chemicals, enzymes, *etc*., for the decomposition of organic matters.

111 These can be metabolized by fermentation process with the support of microorganisms. The

112 lignocellulosic biomass derived bio–H_2 production necessitates the development in commercially

113 and eco–friendly technologies towards the pretreatment process (Hendriks and Zeeman, 2009).

114 In this concern, the lignocellulosic biomass pretreatment techniques on its structure have

115 highlighted herein with the pros and cons of each technique, especially about the cellulose

116 digestibility. This review mainly focuses on novel and advances physical, chemical, physico–

117 chemical, microbiological and nanotechnology based pretreatment techniques towards

118 lignocellulosic biomass pretreatment for bio–H_2 production *via* fermentation.

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120 **2.   Lignocelluloses and pretreatments**

121   The lignocellulosic biomass recalcitrance is mainly depend upon the complex plant cell

122 wall, heterogeneous crystalline cellular components, and the extent of lignification, further these

123 are all the key facts to make the cell resistant/accessible to chemical and bio reagents. Thereby,

124 the recalcitrance of lignocellulosic biomass materials has been done eventually by means of the

125 pretreatment techniques as they hold a prominent role in the utilization of those biomass

126 materials towards industrial applications. Before the downstream process of disintegration of

127 complex lignin structure, using the suitable pretreatment techniques can be employed for

128 reducing the crystallinity and solubilization of hemicellulose content. Thereby, the accessibility

129 of reagents/enzymes and enhancement of their activity over the surface has been increased

130 towards the lignocellulosic biomass materials (Abraham et al., 2020). The suitable pretreatment

131 mainly offers the digestion of cellulose, hemicellulose and lignin moieties of lignocellulosic

132 materials, consequently followed by reduction in size of the lignocellulosic particles. Thus, there

133 is a way to enrich the available surface areas for efficient reagent/enzymatic processes, which

134 can obviously lead to effective conversion /degradation / digestibility of the complex

135 polysaccharides of the lignocellulosic materials into simple monomers and are easily

136 metabolizable / easily producing fermentable sugars to yield bio–H_2. There is further conversion

137 of valuable bio–H_2 while the hydrolytic process with low energy consumption, accompanied by

138 the formation of non–toxic enzyme inhibitors, *etc* (Abraham et al., 2020; Dharmaraja et al.,

139 2019; Mankar et al., 2021; Usmani et al., 2020). Recently, various pretreatment techniques have

140 been employed for dissimilar lignocellulosic materials and each technique possesses its own pros

141 and cons. There are five kinds of pretreatment techniques (Fig. 1) *viz.* (i) physical, (ii) chemical,

142 (iii) physico–chemical / thermo–chemical (iv) biological and (v) nanotechnology based

143 pretreatment techniques (Anu et al., 2020; Ashokkumar et al., 2022; Dharmaraja et al., 2019;

144 Kucharska et al., 2018; Singh et al., 2018), which all are widely been employed for the

145 lignocellulosic materials pretreatment processes. Each technique follows its own characteristic

146 experimental conditions to break the complex structure of lignocellulose materials to yield bio–

147 H_2 and a range of value added products, besides.
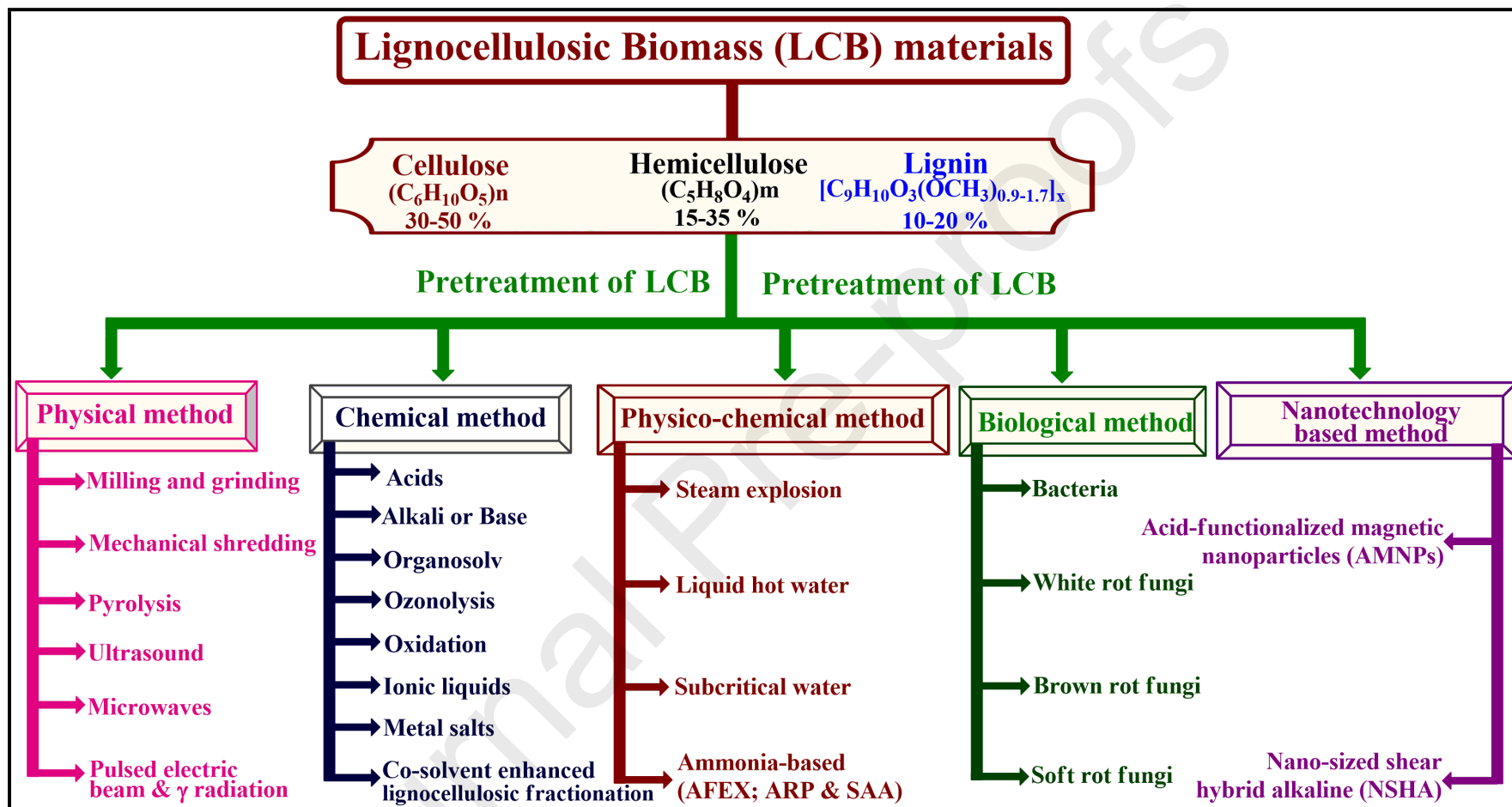
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Fig. 1. Various pretreatment methods for lignocellulosic biomass materials.

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3.1. Lignocellulosic pretreatment by physical methods

The pretreatment by physical processes strongly enhances the hydrolytic efficacy and the decomposition of biomass anaerobically not only to liquid as well as gaseous bio–fuels but also some other value added bio–products (Chandel et al., 2022; Sinha and Pandey, 2011). Abbasi and Abbasi (Abbasi and Abbasi, 2010), has shown the bio–H_2 productivity by means of fermentation possibly increases during mechanical/physical pretreatment. Further, it can be observable that pretreatment by mechanical processes may raise the temperature of biomass materials to about 70 °C. Physical methods for lignocellulosic complex structure mainly include mechanical shredding (grinding *via* chipping, milling); steam explosion & AFEX (Ammonia fiber/freeze expansion), pyrolysis, radiation energy-based microwaves, pulsed electric field and ultrasound techniques.

3.1.1. Mechanical shredding and Pyrolysis

Mechanical shredding (grinding *via* chipping, milling) for soft biomass at a temperature of about 50–70 °C) leads to rupture the lignocellulosic fibers and thereby reduces the period of time duration to digest the materials upto about 23–59% for further treatment to yield fermentative bio–H_2 (Guo et al., 2012; Singh et al., 2022). The fractionation of the shredded materials by means of sieves system makes the particles finer then it consequently leads to an effective hydrolytic process. Further, it can provide nonchemical, green route towards the lignocellulosic pretreatment with no production of unwanted products that assists simultaneously the downstream conversion and processing of the lignocellulosic components (Martin–Sampedro et al., 2012). Though such an overall mechanical pretreatment process is energy–intensive and, thereby one should bring its application for a reasonable raise in the output of final energy only. Pyrolysis is an alternative pretreatment technique for biomass materials but not to produce bio–H_2, instead a mixture of syn–gas and bio–oil (Karimi and Taherzadeh, 2016; Singh et al., 2022). It mainly consists of the thermo–chemical disintegration of biomass materials. Such kind of decomposition begins at about 200 °C.

3.1.3. Irradiation processes

Microwave is a new pretreatment option to deconstruct the lignocellulosic 3D complex structure using microwaves to yield bio–H_2 after suitable fermentation of the biomass. Microwaves applied can be suspended in an acidic (1%, 2% / 3% H_2SO_4 (sulfuric

acid) or alkaline solution NaOH (sodium hydroxide) that results in an effective increase in the extent of delignification of about 12–30 % (Diaz et al., 2013; Singh et al., 2022). The application of microwave radiation for 5 min on sugarcane bagasse with water (distilled), acid of phosphorus (H_3PO_3: pH=3.0) and glycerol of about 10 % indicates that 5.4 % (w/w) fractions of lignin and 11.3 % (w/w) fractions of xylan are disintegrated. In addition, after 24 h of incubation the sugarcane bagasse can be treated with microwaves to achieve a high yield by means of the enzymatic hydrolysis of hemicelluloses (22.4 %) and celluloses (40.2 %) (Singh et al., 2022). The pulsed electric field in the form of γ radiation possesses highly penetrating power (Kortei and Wiafe–kwagyan, 2014; Singh et al., 2022). Thereby, it can be applied to thick materials, and it results in the biomass degradation to overcome biomass recalcitrance, followed by solubility increase and decrease in mechanical strength. Conversely, this technique has not been applied in industrial scale, owing to its costs and environmental as well as some safety issues. Among the non–thermal technologies pulsed electric fields (PEF) is an emerging one though that has not been extensively studied. It is owing to the fact that the precise mechanisms by pulsed electric fields are not well understood. However, to achieve many of these processes require very high treatment intensities, and duration from microseconds to milliseconds may cause temporary effects only (Kortei and Wiafe–kwagyan, 2014; Singh et al., 2022). Moreover, inactivating pulsed electric field is the safety measure as per the International guidelines and national safety standards for electromagnetic fields, which are developed on the basis of the current scientific knowledge. I–γradiation has high potential, though its development and commercialization has been obstructed in the favor of public perceptions. Furthermore, the employment of ultrasonication of frequency 20–40 kHz for biomass pretreatment obviously results in decomposition of the lignocellulosic biomass structures by means of loosening, swelling, and rupturing of fibrils *via* breaking of inter molecular hydrogen linkages (Kucharska et al., 2018) for producing fermentative bio–H_2, more effectively. Conversely, the economic viability on the fermentation to yield bio–H_2 obviously can be led by mechanical pretreatment, correlated to high energy operations for the mechanical biomass chipping fragmentation (Kucharska et al., 2018).

3.2.   Chemical Pretreatment for Lignocellulosic Biomass

Generally, the chemical pretreatment for lignocellulosic biomass (LCB) materials processes are more widely utilized than other physical or biological methods, since, they are more effective as well as enhance the biodegradation of complex LCB materials to yield bio–H_2. The common chemicals such as H_2SO_4, HCl, HNO_3, H_3PO_4, HCOOH, CH_3COOH, NaOH, KOH, $Ca(OH)_2$, $NH_{3(aqu)}$, H_2O_2, *etc.,* are widely utilized in this pretreatment process.

3.2.1. Acid pretreatment

In acid pretreatment method, when the lignocellulosic biomass materials are pretreated with inorganic and organic acids such as HCl, H_2SO_4, HNO_3, H_3PO_4, formic acid, oxalic acid, maleic acid, *etc.,* generate the hydrogen (H^+) ions, which breakdown the glucosidic chain bonds present between long cellulose and hemicellulose chain into simple sugar units (Ashokkumar et al., 2022; Baruah et al., 2018; Sahoo et al., 2018; Solarte–Toro et al., 2019). Generally, the acid pretreatment involves either the addition of concentrated acids (30–70 % at < 100 ^{o}C) or dilute acids (0.2 – 2.5 w/w % or 0.5 – 10 % v/v at 120 – 250 ^{o}C) to the LCB materials (Badiei et al., 2014). Dilute H_2SO_4 pretreatment is commonly used for poplar, switch grass, spruce, and corn stover feedstocks. The conc. acid pretreatment can accelerate a high sugar conversion rate (> 90 %) and these acids are more toxic as well as corrosive in nature. Also, the utilization of conc. acids causes the undesired cellulose degradation that is leading to produce huge amount of inhibitory products such as furfurals, aldehydes, 5–hydroxymethyl furfural and phenolic acids. Also, the recovery of acids after hydrolysis process leads to the further treatment process (Amin et al., 2017). Hence, the effective acid pretreatment process involves the selection of acids as mild or dilute acids can be utilized to breakdown the LCB materials into high conversion rate of sugar unit in an economical as well as environmental friendly manner with low generation of inhibitors (Baruah et al., 2018; Ravindran and Jaiswal, 2016; Sahoo et al., 2018; Zheng et al., 2014). Sahoo et al., (Sahoo et al., 2018) reported the effect of dilute H_2SO_4 (0.4 %) and NaOH (1 %) pretreatment on wild rice grass (*Zizania latifolia*) for enzymatic hydrolysis and showed 163 and 92 mg sugar g^{-1} respectively. This study proves the dilute mineral acids pretreatment process is more effective than alkali methods. Furthermore, the organic acids such as oxalic, maleic, citric and formic acids are more efficient than dilute mineral acids for LCB pretreatment for efficient industrial scale fermentative production of bio–H_2 (Baruah et al., 2018).

3.2.2. Alkaline pretreatment

Alkaline or base pretreatment involves the addition of alkaline reagents or bases (such as NaOH, KOH, Ca(OH)$_2$, NH$_4$OH, *etc*) to lignocellulosic biomass materials leading to an increase of internal surface by swelling, decrease of cellulose crystallinity & polymerization, destruction of chemical links between lignin and other polymer units i.e., cleavage of ester and other linkages between lignin and hemicellulose or other carbohydrate moieties, lignin breakdown, solvation of hemicellulose *etc* (Amin et al., 2017; Ashokkumar et al., 2022; Kim et al., 2016; Nahak et al., 2022), as a result a high conversion hydrolysis rate of cellulose into fermentable sugar units either by enzymatic or microorganisms hydrolysis. Generally, the alkaline pretreatment is more effective for hardwood, agricultural residues, herbaceous crops, *etc* with low content of lignin. However, the excessive use of NaOH may cause inhibition of anaerobic digestion (AD) process, especially by methanogenesis and also leads to soil salination as well as water pollution (Kumari and Singh, 2018). Yuan et al. (Yuan et al., 2018), investigated the NaOH and Na$_2$CO$_3$ pretreatments on wheat straw at 0 °C for 6 h and showed a solid dissolution efficiency of 86.7 and 91.1 %, respectively. They also showed an improved lignin solubilization as well as hydrolysis of cellulose and hemicellulose that obviously leads to increase the biogas generation. Shen et al., (Shen et al., 2017) reported that NaOH pretreatment on vinegar residue (VR) showed an increased CH$_4$ yield (205.86 mL g^{-1} at 3% NaOH), that is 54 % higher than the untreated VR. Zhu et al.,(Zhu et al., 2010) reported that over 37 % of biogas can be produced from corn stover by NaOH pretreatment than untreated ones. Shah and Tabassum (Shah and Tabassum, 2018) investigated the lime [Ca(OH)$_2$] pretreatment on corn cob residue accelerates the digestion process followed by removal of lignin and enhances the biogas productions to 2 times higher than the untreated ones. The major benefit of alkaline pretreatment is efficient for removal of hemicellulose and lignin, to increase the surface area for further hydrolysis process, but this pretreatment causes several issues, especially long process time, difficult reclamation of salt formation, the black liquor and high energy input for hydrolysis (Ashokkumar et al., 2022; Shirkavand et al., 2016; Vu et al., 2020). Effects of acidic and alkaline pretreatments on bio–H$_2$ production are given in Table 1.

289 Table 1. Effects of acid and alkali on bio–H_2 production through inoculum pretreatment [Adopted from modified Ref. (Bundhoo et al.,
290 2015)].

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Inoculum pretreatment	Pretreatment Conditions	Yield of bio–H_2	References
Anaerobic inoculum	Substrate: Glucose	Control: 1.54 meq mol^{-1} glucose	(Chaganti et al., 2012)
	Acid: 2.0 M HCl	Treated: 3.00 meq mol^{-1} glucose	
	pH: 3.0 (24 h)	Yield : + 94.80 %	
	Substrate: Glucose	Control: 1.54 meq mol^{-1} glucose	
	Alkali: 3.0 M NaOH	Treated: 2.80 meq mol^{-1} glucose	
	pH: 11.0 (24 h)	Yield : + 81.80 %	
Activated sludge	Substrate: Glucose	Control: 0.38 mol mol^{-1} glucose	(S. Chang et al., 2011)
	Acid: 1 M HCl	Treated: 1.51 mol mol^{-1} glucose	
	pH: 3.0 (24 h)	Yield : + 297.40 %	
	Substrate: Glucose	Control: 0.38 mol mol^{-1} glucose	
	Alkali: 1 M NaOH	Treated: 1.34 mol mol^{-1} glucose	
	pH: 10.0 (24 h)	Yield : + 252.60 %	
Anaerobic inocula	Substrate: Glucose	*Without pre–acidification*	(Cheong and Hansen, 2006)
	Acid: $HClO_4$	Control: 60.5 ml	
	pH: 2.0 (10 min)	Treated: 311.0 ml	
		Yield : + 414.0 %	

		With Pre–acidification (10 M HCl)	
		Control: 32.6 ml	
		Treated: 320.2 ml	
		Yield : + 882.20 %	
Sludge	Substrate: Glucose	Control: 0.7 mol mol^{-1} glucose	(Elbeshbishy et al., 2010)
	Acid: 1 N HCl	Treated: 1.11 mol mol^{-1} glucose	
	pH: 3.0 (24 h, 4 ^{o}C)	Yield : + 58.60 %	
	Substrate: Glucose	Control: 0.7 mol mol^{-1} glucose	
	Alkali: 1 N NaOH	Treated: 0.68 mol mol^{-1} glucose	
	pH: 10.0 (24 h, 4 ^{o}C)	Yield : – 2.90%	
	Substrate: Corn stover hydrolysate	Control: 2.7 mmol g^{-1} sugar $_{used}$	(Zhang et al., 2011)
	Acid: 1.0 M HCl	Treated: 3.21 mmol g^{-1} sugar $_{used}$	
	pH: 3.0 (24 h)	Yield : + 18.90 %	
	Substrate: Corn stover hydrolysate	Control: 2.7 mmol mmol g^{-1} sugar$_{used}$	
	Alkali: 1.0 M NaOH	Treated: 4.45 mmol mmol g^{-1} sugar$_{used}$	
	pH: 12.0 (24 h)	Yield : + 64.80 %	
Methanogenic granules	Substrate: Glucose	Control: 0.42 ml g^{-1} glucose	(Hu and Chen, 2007)
	Acid: 0.1 N HCl	Treated: 0.00 ml g^{-1} glucose	
	pH: 3.0 (24 h)	Yield : – 100.00 %	
Sewage sludge	Substrate: Glucose	Control: 124.99 ml g^{-1} glucose	(Hu and Chen, 2007)

	Acid: 0.1 N HCl	Treated: 89.01 ml g^{-1} glucose	
	pH: 3.0 (24 h)	Yield : – 28.80 %	
Marine intertidal sludge	Substrate: Glucose	Control: 0.2 mol mol^{-1} glucose	(Liu et al., 2009)
	Acid: 1 M HCl	Treated: 0.86 mol mol^{-1} glucose	
	pH: 3.0 (10 min, 12 h acclimation)	Yield : + 330.00 %	
	Substrate: Glucose	Control: 0.2 mol mol^{-1} glucose	
	Acid: 1 M NaOH	Treated: 0.11 mol mol^{-1} glucose	
	pH: 12.0 (10 min, 12 h acclimation)	Yield : – 45.00 %	
Anaerobic sludge	Substrate: Cassava stillage	*Batch system*	(Luo et al., 2010)
	Acid: 2.0 N HCl	Control: 65.3 ml g^{-1} volatile solids (VS)	
	pH: 3.0 (24 h)	Treated: 46.5 ml g^{-1} VS	
		Yield : – 28.80 %	
	Substrate: Cassava stillage	*Batch System*	
	Alkali: 2 N NaOH	Control: 65.3 ml g^{-1} volatile solids (VS)	
	pH: 12.0 (24 h)	Treated: 59.0 ml g^{-1} VS	
		Yield : – 9.60 %	
	Substrate: Palm oil mill effluent	Control: 0.12 mmol g^{-1} chemical oxygen demand (COD)	(Mohammadi et al., 2011)
	Acid: 6.0 N HCl		
	pH: 3.0 (24 h)	Treated: 0.32 mmol g^{-1} COD	
		Yield : + 166.70 %	

	Substrate: Palm oil mill effluent	Control: 0.12 mmol g^{-1} COD	
	Alkali: 6.0 N NaOH	Treated: 0.37 mmol g^{-1} COD	
	pH: 12.0 (24 h)	Yield : + 208.30 %	
	Substrate: Glucose	Control: 178.6 ml	(Yin et al., 2014)
	Acid: 1.0 M HCl	Treated: 227.2 ml	
	pH: 3.0 (24 h, 25 °C)	Yield : + 27.20 %	
	Substrate: Glucose	Control: 178.6 ml	
	Alkali: 1.0 M NaOH	Treated: 402.6 ml	
	pH: 10.0 (24 h, 25 °C)	Yield : + 125.40 %	
Anaerobic granulated sludge	Substrate: Palm oil mill effluent	Control: 11.31 mL g^{-1} COD	(Mohammadi et al., 2012)
	Acid: 6.0 N HCl	Treated: 16.38 mL g^{-1} COD	
	pH: 3.0 (24 h)	Yield : + 44.8%	
	Substrate: Palm oil mill effluent	Control: 11.31 mL g^{-1} COD	
	Alkali: 6.0 N NaOH	Treated: 17.81 mL g^{-1} COD	
	pH: 12.0 (24 h)	Yield : + 57.50 %	
Anaerobic digested sludge	Substrate: Sucrose	*First batch*	(O–Thong et al., 2009)
	Acid: 1.0 M HCl	Control: 0.14 mol mol^{-1} hexose	
	pH: 3.0–4.0 (24 h)	Treated: 0.43 mol mol^{-1} hexose	
		Yield : + 207.10 %	
		Second batch	

		Control: 0.3 mol mol^{-1} hexose	
		Treated: 0.65 mol mol^{-1} hexose	
		Yield : + 116.70 %	
	Substrate: Sucrose	*First batch*	
	pH: 12.0 (24 h)	Control: 0.14 mol mol^{-1} hexose	
		Treated: 0.3 mol mol^{-1} hexose	
		Yield : + 114.30 %	
		Second batch	
		Control: 0.3 mol mol^{-1} hexose	
		Treated: 0.51 mol mol^{-1} hexose	
		Yield : + 70.00 %	
Granular anaerobic culture	Substrate: Glucose	Control: 0.14 mol mol^{-1} glucose	(Pendyala et al., 2012)
	Acid: 2.0 N HCl	Treated: 1.10 mol mol^{-1} glucose	
	pH: 3.0 (24 h)	Yield : + 685.70 %	
	Substrate: Glucose	Control: 0.14 mol mol^{-1} glucose	
	Alkali: 3.0 M KOH	Treated: 0.83 mol mol^{-1} glucose	
	pH: 12.0 (24 h)	Yield : + 492.90 %	
Flocculated anaerobic culture	Substrate: Glucose	Control: 1.3 mol mol^{-1} glucose	(Pendyala et al., 2012)
	Acid: 2.0 N HCl	Treated: 1.59 mol mol^{-1} glucose	
	pH: 3.0 (24 h)	Yield : + 22.30 %	

	Substrate: Glucose Alkali: 3.0 M KOH pH: 12.0 (24 h)	Control: 1.3 mol mol^{-1} glucose Treated: 1.41 mol mol^{-1} glucose Yield : + 8.50 %	
Sludge from slaughterhouse	Substrate: Sucrose Acid: 1.0 N HCl pH: 3.0 (24 h) Substrate: Sucrose Acid: 1.0 N HCl pH: 3.0 (24 h)	Control: 1.0 mol mol^{-1} sucrose Treated: 2.0 mol mol^{-1} sucrose Yield : + 100.00 % Control: 0.7 mol mol^{-1} sucrose Treated: 1.0 mol mol^{-1} sucrose Yield : + 42.90 %	(Penteado et al., 2013)
Mixed microbial culture	Substrate: Glucose Acid: 1.0 N HCl pH: 3.0 (24 h) Substrate: Glucose Alkali: 1.0 N NaOH pH: 11.0 (24 h)	Control: 180.4 ml Treated: 51.9 ml Yield : – 71.20 % Control: 180.4 ml Treated: 134.1 ml Yield : – 25.70 %	(Ren et al., 2008)
Anaerobic sludge consortium	Substrate: Residual glycerol from biodiesel synthesis Acid: 1.0 M HCl pH: 3.0 (24 h) Substrate: Residual glycerol from biodiesel	Control: 1.20 % mol g^{-1} glycerol Treated: 0.49 % mol g^{-1} glycerol Yield : – 59.20 % Control: 1.20 % mol g^{-1} glycerol	(Rossi et al., 2011)

		Treated: 0.03 % mol g^{-1} glycerol	
	Alkali: 1.0 M NaOH	Yield : – 97.50 %	
	pH: 10.0 (24 h)		
Anaerobic mixed microflora	Substrate: Dairy wastewater	Control: 0.0018 mmol g^{-1} COD	(Venkata Mohan et al., 2008)
	Acid: H_3PO_4	Treated: 0.0079 mmol g^{-1} COD	
	pH: 3.0 (24 h)	Yield : + 338.90 %	
Digested sludge	Substrate: Glucose	Control: 65.7 ml	(Wang and Wan, 2008)
	Acid: 1.0 M HCl	Treated: 96.8 ml	
	pH: 3.0 (24 h)	Yield : + 47.30 %	
	Substrate: Glucose	Control: 65.7 ml	
	Alkali: 1.0 M NaOH	Treated: 125.9 ml	
	pH: 10.0 (24 h)	Yield : + 91.60 %	

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3.2.3. Organosolv pretreatment

The most effective and promising organosolv or organic solvent pretreatment method is performed by the aqueous organic solvents such as alcohols (methanol, ethanol, butanol), acetone, phenol, ethylene glycol, tetrahydrofurfuryl alcohol, *etc* with / without addition of a small amount of inorganic acid catalyst (H_2SO_4, HCl, oxalic acid) for stimulating the pretreatment efficiency of lignocellulosic biomass materials at specified temperature and pressure (Ashokkumar et al., 2022; Capolupo and Faraco, 2016; Khan et al., 2022; Naik et al., 2021; Ravindran and Jaiswal, 2016). This pretreatment completely removes or solubilizes the hemicellulose and lignin moieties in the LCB but the cellulose fraction remains unaffected during this process *i.e.,* to cleave the linkage of lignin and hemicellulose fractions, which can increase the pore volume and accessible surface area of cellulose. As a result, the lignin moieties are dissolved in the organic solvent phase, while cellulose is recovered as solid (Amiri et al., 2014). In general, lower EtOH / H_2O ratios favor the hemicellulose hydrolysis and enzymatic degradability of pretreated LCB since EtOH inhibits the performance of hydrolytic enzymes. The ethanosolv pretreatment with H_2SO_4 on saccharification of poplar biomass has released upto 78 % of the polysaccharides (Chu et al., 2021). Koo et al., (Koo et al., 2011) investigated the aqueous EtOH (50 % v/v) with 1 % NaOH on *Liriodendron tulipifera* (Tullip tree) at 150 °C for 50 min and showed an increased bioethanol production (after hydrolysis and fermentation steps) significantly to 96 %. Sarkar et al., utilized birch sawdust to pretreat at 200 °C within time duration 15 min. In an air–heated reactor, they mixed the sawdust in 60% ethanol and 1% H_2SO_4 (w/w biomass). The pretreated contents then were separated by means of vacuum filtration from the slurry. Consequently, washed with 1.1 L 60% of v/v ethanol/water mixture and finally dried in an oven at 50 °C, overnight. The collected filtrate was used to produce acidogenic fermentative green bio–H_2 (121.4 mL/gVS) (Sarkar et al., 2022). By comparing with other pretreatments, organosolv pretreatment process has many advantages such as ease of recovery of solvents by distillation, low environmental impact, and recovery of high quality lignin as high value added by–product.

3.2.4. Ozonolysis pretreatment

In this pretreatment method, the powerful oxidant say ozone (O_3) is sparged into LCB materials, the lignin and hemicellulose contents are degraded but the cellulose fraction is not at all affected (Bensah and Mensah, 2013; Kucharska et al., 2018). The lignin is now

334 oxidized into soluble low molecular weight carboxylic acid compounds such as AcOH,

335 HCOOH, *etc*. The efficiency of enzymatic hydrolysis treatment of LCB by O_3 has enhanced

336 upto 5–folds and also forms no toxic hydrolysis end–products. Silverstein et al., (Silverstein

337 et al., 2007) studied the ozone pretreatment of cotton stalk (10 5 w/v; Temp. 4 °C; Time 30–

338 90 min) showed the reduced lignin content of 11.97–16.60 % and the solubilization of xylan

339 (1.9–16.7 %) and glucan (7.2–16.6 %), which is comparatively lower by this treatment than

340 alkali NaOH process. The great merit for this pretreatment method is no generation of

341 inhibitors i.e., any toxic residues are not generated, however, this method is more expansive

342 than the others. García–Cubero et al., (García–Cubero et al., 2009) reported the improved

343 enzymatic hydrolysis yields of wheat and rye straw upto 89% and 57% respectively, while

344 for the untreated wheat and rye straw the enzymatic hydrolysis yields were 29 % and 16 %

345 respectively.

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347 ### *3.2.5. Oxidation pretreatment*

348 In this method, the powerful oxidizing agents like hydrogen peroxide (H_2O_2) or

349 alcoholic solution of peracidic acid are widely being employed for the pretreatment of LCB

350 materials i.e., the oxidant completely dissolves the lignin and amorphous cellulose, while

351 hemicellulose fractions undergo dissolution but the crystalline cellulose content is not

352 dissolved in it (Kucharska et al., 2018). The LCB materials with H_2O_2 generate $^\bullet$OH radicals,

353 which vigorously oxidize as well as degrade lignin fraction. The optimal dosage of H_2O_2 is

354 2.15 % (v/v) at 35 °C and showed effective hydrolysis of LCB materials (Kucharska et al.,

355 2018). The wet oxidation pretreatment of lignocellulosic biomass is done at 195 °C for 10–20

356 min (Anu et al., 2020) with the help of an oxidizer. This pretreatment method is a rapid and

357 effective processes but the formation of inhibitors during fermentation process is its main

358 demerit. The whole hemicellulose and ~ 50 % of lignin fractions present in the LCB materials

359 have been solubilized by treatment with 1–2 % H_2O_2 at temperature of 25–30 °C. Pedersen

360 and Meyer (Pedersen and Meyer, 2009) studied the pretreated of wheat straw with wet

361 oxidation method and showed the yield of 400 and 200 g/kg dry matters for glucose and

362 xylose fractions, respectively followed by enzymatic hydrolysis at 50 °C after 24 h.

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364 ### *3.2.6. Ionic liquids (ILs) pretreatment*

365 Ionic liquids (ILs) are thermally stable organic salts composed of cations (such as

366 imidazolium, aliphatic ammonium, pyridinium, alkylated phosphonium, sulfonium ions, *etc*)

and anions (such as acetate, chloride, bromide, sulphate, methanoate, nitrate, sulphate, triflate, *etc*) in the liquid state with lower melting point (< 100 ^{o}C) and low vapour pressure, as well (Baruah et al., 2018; Behera et al., 2014; Bensah and Mensah, 2013; Brandt et al., 2013; Yoo et al., 2017). ILs is also act as green solvents (GSs) because they possess low vapour pressure, melting point, non–volatility, non–toxicity, high thermal and chemical stability, *etc* (Yoo et al., 2017). During the ILs pretreatment process, both anions and cations form a strong inter– and intramolecular hydrogen bonding with cellulose and other carbohydrate hydroxyl groups in the LCB materials. As a result, the cellulose moiety dissolution increases in presence of electron–withdrawing groups in the alkyl chains of IL cations, hence, the cellulose moiety can undergo precipitation and the lignin can be dissolved in ILs (Chen et al., 2017; Yoo et al., 2017). Some of the ILs like 1–ethyl–3–methylimidazolium diethyl phosphate–acetate, 1–butyl–3–methylimidazoliumacetate, 1–butyl–3–methylimidazoliumchloride, 1–butyl–3–methylimidazoliumacetate, 1–benzyl– 3–methylimidazoliumchloride, 1–butyl–3–methylimidazoliummethylsulfate, 1–ethyl–3–methylimidazoliumgroups, 1,3– dimethylimidazolium groups, cholinium amino acids, cholinium acetate, 1–allyl–3–methylimidazolium chloride, *etc*., are widely utilized for the treatment of rice husk, water hyacinth, rice straw, kenaf powder, poplar wood, wheat straw, and pine (Behera et al., 2014; Brandt et al., 2013; Kucharska et al., 2018; Shirkavand et al., 2016). The most popular IL is imidazolium–based salts namely Amimcl (1–allyl–3–methylimidazolium chloride) and Bmimcl (1–butyl–3–methylimidazolium chloride), which may be effectively applied for cellulose dissolution when the temperature is < 100 ^{o}C (Baruah et al., 2018; Kucharska et al., 2018). Zhi–Guo and Hong–Zhang (Zhang Zhi–guo, 2012) studied the pretreatment of wheat straw with Amim–Cl and showed 100 % increase in glucose yield, when the temperature was increased from 125 to 150 ^{o}C at 2 h. Das et al., (Das et al., 2021) reported the enzymatic hydrolysis and ethanol fermentation of several wood materials with two different ionic liquids namely cholinium lysinate [Ch][Lys] and ethanolamine acetate [EOA] [OAc] generated 24–84 % of glucose and 14–80 % of xylose. Rahim et al., (Rahim et al., 2020) investigated the combination of ultrasound irradiation and three different ILs [Emim][OAc], [Emim] [Cl], [Emim][HSO$_4$] pretreatment of bamboo provided 63.99 % of cellulose and 14.99 % of lignin.

3.2.7. Metal salts pretreatment

The metal salts pretreatment of LCB materials requires a high pressure reactor i.e., the biomass materials are loaded in the reactor along with the metal chlorides such as $ZnCl_2$, $FeCl_3$, $FeCl_2$, $CrCl_2$, $MnCl_2$, $AlCl_3$, *etc* and then heated to 170–180 °C for 20–30 min (Ravindran and Jaiswal, 2016). In addition, the pretreated excess metal salts and other solids are removed by superfine filtration process. Chen *et al.,* (Chen et al., 2014) studied the pretreatment of bagasse with metal chlorides in dilute acidic medium followed by enzymatic hydrolysis and showed a decrease in the total mass of the substrate and most of the sugar moieties are degraded in the acid environment and a major share of them can be appeared in the effluent. Wang et al., (Wang et al., 2014) investigated the hydrolysis of bamboo biomass by dil. HCl in the presence of 1–butyl–3–methylimidazolium chloride with Cu^{2+} ion showed a maximum sugar yield of 67.1 % at 100 °C.

3.2.8. Co–solvent enhanced lignocellulosic fractionation (CELF)

In this CELF method, a mixture of tetrahydrofuran (THF) and H_2O is utilized as a monophasic solvent system. This pretreatment process involves the delignification followed by conversion of glucose–rich LCB materials into high value–added fuels, including 5–hydroxymethyl furfural (5–HMF), furfural and levulinic acid (LA) (Ashokkumar et al., 2022). Patri et al., 2021 (Patri et al., 2021) studied the THF co–solvent with mineral H_2SO_4 (act as catalyst) on enzymatic hydrolysis of switchgrass biomass, yielded approximately 90 % glucose at 160 °C.

3.3. Physico–chemical pretreatment

Among physico–chemical pretreatments such as steam explosion (SE), liquid hot water (LHW), subcritical water (SCW) and ammonia–based methods are promising to breakdown the recalcitrant structure of LCB materials. The liquid hot water and steam explosion processes release very high concentrations of degradation compounds *viz*. furfural, 5–hydroxymethylfurfural, acetic acid, formic acid and phenolic compounds that can inhibit enzymes as well as fermentative microorganisms (Anu et al., 2020; Ravindran and Jaiswal, 2016). The steam explosion (SE) or autohydrolysis is one of the oldest and effective methods for enzymatic hydrolysis of LCB materials; the LCB materials are pretreated to a high steam pressure (0.7–4.8 MPa) and temperature (160–206 °C) for 1–20 min. At very high temperature and pressure, the steam explosion as well as AFEX (ammonia fiber explosion)

433 can easily disintegrate the cellular components by means of lignocellulosic biomass digestion

434 to yield valid fermentable sugars (Banoth et al., 2017). The main demerit of this steam

435 explosion is the partial degradation of hemicelluloses and thereby producing toxic products.

436 Similar way, the AFEX technique has been considered as efficient process with low content

437 of lignin that is the drawback of this pretreatment process (Sun et al., 2002). Baral and Shah

438 (Baral and Shah, 2017) reported the steam explosion pretreatment of corn stover to produce

439 113.5 million liters butanol per year. Barbanera et al., (Barbanera et al., 2015) investigated

440 the glucose yield on olive tree prunes through steam explosion method, the maximum glucose

441 yield, up to 86 % was achieved at experimental conditions (Temp.: 201 ^{o}C, Pressure: 0.86

442 MPa; Time: 15 min). Vivekanand et al., (Vivekanand et al., 2014) reported the combined

443 sequential SO_2 with steam explosion methods, followed by enzymatic hydrolysis that showed

444 more effective polysaccharide conversion upto of 81 %. The LHW pretreatment is an ideal

445 method for the lignocellulose substrates where the addition of chemicals for delignification

446 can result in effective utilization of the biomass. The process is performed only in the

447 customized high pressure reactor. This method is similar to the steam explosion method and

448 this method does not require corrosion resistant reactors or any chemicals and there is no

449 formation of toxic components (Jiang et al., 2015; Ravindran and Jaiswal, 2016). Muharja et

450 al. (Muharja et al., 2018) studied the combined green process of subcritical water (SCW) and

451 enzymatic hydrolysis for bio–H_2 fermentation from coconut husk and the maximum bio–H_2

452 yield, up to 0.279 mol/mol by consumption of sugar, which is lower than the other works.

453 Further, ammonia (NH_3) is an effective agent for the pretreatment of LCB materials. There

454 are three different ammonia–based methods namely (i) ammonia fiber explosion (AFEX), (ii)

455 ammonia recycled percolation (ARP) and (iii) soaking aqueous ammonia (SAA). The AFEX

456 method is a novel advancement technology for the production of fermentable simple sugar

457 units from LCB materials over conventional alkaline processes (Naik et al., 2021; Raj et al.,

458 2022; Ravindran and Jaiswal, 2016). Also, the AFEX pretreatment is most appropriate

459 method for preventing cellulase adsorption to lignin. The AFEX process can be efficiently

460 employed for low–lignin LCB materials like switchgrass, corn stover, Miscanthus, *etc*.,

461 showed > 90 % of glucose yield, during simultaneous saccharification and fermentation

462 process. After the completion of pretreatment, the vaporized NH_3 has been collected,

463 recycled and reused again. Jin et al (Jin et al., 2016) reported that the Great Lakes Bioenergy

464 Laboratories in the US have demonstrated the AFEX pretreatment method for cellulosic

465 ethanol production, which reduced enzyme loading by 66 % and also increased EtOH

466 productivity by 129 %. In an ARP pretreatment process, the poplar wood is soaked in 15 %

467 of $NH_{3\ (aqu.)}$ for 1 h at 40 °C and the pressure was increased to 20 bar. After increasing the

468 temperature upto 180 °C, more liquid extracting was percolated at the rate of 3 ml/min for 90

469 min. In this ARP method, the removal of lignin has been achieved 87 % (Naik et al., 2021).

470 The SAA method also reduces or partially eliminates the lignin fraction from LCB materials.

471

3.4. Biological pretreatment

473 Biological pretreatment process is more superior to the other methods (Anu et al.,

474 2020) because this method offers numerous advantages such as low energy, low capital cost,

475 decreases in the dependence on chemicals, *etc.,* but main disadvantage is the low hydrolysis

476 rate. During the biological pretreatment of LCB materials, the microorganisms such as

477 bacteria, fungi, enzymes, metabolites from enzymes, *etc* are playing a vital role before the

478 enzymatic hydrolysis of LCB components (Dey et al., 2022; Hassan et al., 2018). The key

479 biological processes are delignification and saccharification. Generally, the microorganisms,

480 such as brown, white, and soft rot fungi have widely been utilized to degrade the LCB

481 materials to produce fermentative bio–H_2 (Dey et al., 2022; Hassan et al., 2018). Certain

482 microorganisms are present in nature, which exhibit cellulolytic and hemicellulolytic

483 abilities. White rot is able to degrade lignin moieties, present in the LCB materials, which is

484 due to the presence of lignin degrading enzymes like peroxidases and laccases. Brown rot

485 commonly attacks the cellulose content, whereas white as well as soft rot target both lignin

486 and cellulose contents of LCB. Furthermore, the soft rot fungi are efficiently degrading the

487 wood polysaccharides however; the alteration of lignin is limited extent only. The commonly

488 utilized white rot fungi like *Cyathus stercoreus, Phanerochaete chrysosporium, Pleurotus*

489 *ostreatus, Ceriporiopsis subvermispora, Ceriporia lacerata, Pycnoporus cinnabarinus,*

490 *Cyathus stercolerus, Cyathus cinnabarinus*, *Ceriporia lacerata, Ceriporiopsis*

491 *subvermispora, Pycnoporus cinnabarinus, Pleurotus ostreatus, Trametes pubescens, etc.,* are

492 frequently applied to degrade lignin because these species contain lignin degradation

493 enzymes, including peroxidase and laccase (Anu et al., 2020; Hassan et al., 2018). In addition

494 to some *Basidiomycetes* species, such as *Bjerkandera adusta, Irpex lacteus, Fomes*

495 *fomentarius,* and *Trametes versicolor* are widely utilized for breaking down of the

496 lignocellulosic materials (Peng et al., 2012). The degradation of lignin by lignolytic enzymes,

497 such as lignin peroxidase, manganese peroxidase and versatile peroxidase, are generated from

498 various microorganisms, which also degrading the lignin structure completely by increasing

the phenolic compounds (Baruah et al., 2018; Raj et al., 2022). Suhara et al.,(Suhara et al., 2012) studied the pretreatment of the bundles of bamboo with *Punctularia* sp. and showed an enhanced in the total sugar upto 60.3 % at the same time the lignin content was also reduced. Chang *et al.,* (K. L. Chang et al., 2011) investigated the enzymatic hydrolysis of rice straw with xylanase and cellulase showed a high hydrolysis yield of 84 % with productivity of 371.91 g glucose/kg of dry rice straw. Recently, the isolated thermophilic *Thermoanaerobacterium* sp. strain F6 produced 1822.6 and 826.3 mL H_2/L of hydrogen using corn cob and sugarcane bagasse respectively (Jiang et al., 2019).

3.5. Nanotechnical pretreatment

Nanotechnology–based pretreatment on lignocellulosic biomass structures is an important methodology to yield bio–H_2. Since the reagents can be easily recycled and reutilized, so it reduces the cost of the process (Chandel et al., 2022). The type of acid–functionalized magnetic nanoparticles (AMNPs) is applicable to the pretreatment of LCB. The AMNPs utilization to enzymatic immobilization, functionalization by means of microbes/chemicals is an alternative to the traditional pretreatment techniques for lignocellulosic biomass. Reusable nature of AMNPs and enzymes obviously is the cost–effective and eco–friendly systems. Nano–sized shear hybrid alkaline (NSHA) catalysts also often utilized for pretreatment techniques for lignocellulosic biomass. The nano–sized metal particles enter into the lignocellulosic cell wall, thereby interaction with biomass component molecules to generate carbohydrates (Abdul Razack et al., 2016; Amin et al., 2017).

3.5.1. AMNPs pretreatment

AMNPs possess higher affinity for hydrolyzed lignocellulosic biomass materials, these are also named as solid acid nanocatalysts. Their reusability with strong magnetic nature has added beneficial role in chemical techniques (Peña et al., 2014). By the year of 2011, sulfonated MNPs were synthesized to hydrolyse the lignocellulosic biomass structure. Similarly, such functionalized MNPs significantly possess better stability and enhance the catalysis process for bio–fuel production (Wang et al., 2020) .

3.5.2. NSHA pretreatment

NSHA catalysts mainly involve in a nano range application, thereby a high shearing of lignocellulosic biomass materials can be performed to remove the lignin molecules for

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532 degradation. It has been suggested that NSHA system plays an important role in both
533 saccharification and refineries. Functionalization of NSHA system can be enhanced with
534 certain additives namely PDAC [Poly(diallyldimethylammonium chloride)] and are utilized
535 in the degradation of lignocellulosic biomass constituents. Such kind of produced charged
536 components function as polyelectrolytes to modify surface of the cellulose and thereby
537 stabilization of the lignin occurs. It has been shown that there is generation of globular
538 complexes with lignin components by means of PDAC, and it can alter the biomass cell wall
539 morphology. Further, the PDAC polyelectrolyte reduces utilization of chemical reagents
540 necessitated by the pretreatment of lignocellulosic biomass constituents (Dey et al., 2022).

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542 ### 3.6. Role of nano–materials in bio–H$_2$ production

543 Production of bio–H, using nano–materials in the bio–fuel industry is very attractive
544 owing to its effective recovery of products (Dey et al., 2022). In such case, the reactions can
545 be performed by metal nano particles (NPs) like Ni(nickel)/Fe(iron) materials. These nano–
546 materials can act as cofactors (like hydrogenase), consequently reduces the exchange of
547 H$^{(+)}$(protons) (Dey et al., 2022). The function of the microbes has been greatly influenced by
548 increasing the metal NPs concentration to yield bio–H. Such a nano–approach improves the
549 rate of e$^{(-)}$ (electron) transfer that suitably improves the metabolic activity of the micro–biota.
550 It has also been demonstrated that the metal NPs can improve the production of bio–H$_2$ in
551 acidic pH, moreover the substrate concentration increases with decrease of bio–H$_2$
552 production, *i.e.*, inverse effect. It was found that the metal oxide NPs can increase 4.5 times
553 of the bio–H$_2$ production, as compared to normal synthetic processes. Similar way with iron
554 NPs (0.2 g/L), nearly a 33% increase in the bio–H$_2$ production was observed in sugar
555 (sucrose) medium (Han et al., 2016). Further, 260% conversion of sugar composition by
556 means with a combination of lignocellulosic substrates and Ti(titanium) NPs. Though, the
557 impact on dark fermentation of bio–H$_2$ production by means of nano–material is still not
558 known clearly (Dey et al., 2022). Further, the main disadvantage of valuable nano–materials
559 assisted technique is its slow rate of yield. It was found that nearly about 35% of
560 lignocellulosic components only converted effectively to bio–H$_2$ and the residues produce
561 some other by–products. Thereby, there a necessity is to upgrade the technique for industrial
562 production of bio–H$_2$ by lignocellulosic substrates *via* improvement/introduction of suitable
563 strain as well as nano–materials.

564

565 **Table 2.** **Production of bio–H₂ by NPs from lignocellulosic materials (Adopted**

566 **and modified from Ref.** (Dey et al., 2022).

567

Nanomaterials	Microbes / Natural substrate or enzyme used	Bio–Hydrogen production	References
Iron	*Enterobacter* sp. and *Clostridium* sp. / Grass	80.70 ml / h, 73.10 %	(Yang and Wang, 2018)
	Mesophilic culture / Starch	200.00 %	(Taherdanak et al., 2016)
	Anaerobic sludge / Sugarcane bagasse	69.00 %	(Reddy et al., 2017)
	Enterobacter aerogenes / Cassava starch	92.00 %	(Lin et al., 2016)
	Anaerobic sludge bacteria / Molasses waste	43.00 %	(Gadhe et al., 2015)
	Thermophillic anaerobic mixed culture / Glucose	53.60 %	(Engliman et al., 2017)
	Anaerobic mixed bacteria / Glucose	33.70 %	(C. Jia et al., 2017; J. Jia et al., 2017)
	Enterobacter cloacae / Glucose	130.00 %	(Nath et al., 2015)
	Clostridium butyricum / Sucrose	32.64 %	(Han et al., 2011)
	Rhodobacter sphaeroides / malate	19.40 %	(Bao et al., 2013)
Nickel	*Bacillus anthracis* / Palm oil mill eluent	151.00 %	(Mishra et al., 2018)
	Anaerobic sludge bacteria / Molasses waste pH =5.6, T=30–35 °C with 0.0567 wt % of Ni NPs / glucose	24.00 % 22.00 % 2.54 mol	(Gadhe et al., 2015; Mullai et al., 2013)
Carbon	Anaerobic mixed bacteria / Glucose (Composite type of carbon)	33.70 %	(C. Jia et al., 2017; J. Jia et al., 2017)
	Anaerobic sludge/ Glucose (nanotube form of carbon)	50.00 %	(Singh et al., 2018)
	Anaerobic sludge / Sucrose (activated carbon)	62.50 %	(Wimonsong and Nitisoravut, 2015)
	Anaerobic sludge / Sucrose (nano	70.00 %	(Bhatia et al., 2021;

	activated carbon)		Wimonsong and Nitisoravut, 2014)
Noble metals	Silver NPs with *Clostridium butyricum* / Glucose	67.50 %	(Zhao et al., 2013)
	Gold NPs with Anaerobic sludge / Acetate	–	(Khan et al., 2013)
	Silver with *Clostridium butyricum*/ Glucose	38.00 %	(Beckers et al., 2013; Singhvi and Kim, 2020)
Palladium	Mixed culture / Glucose	9.00 %	(Mohanraj et al., 2014)
Titanium	Anaerobic sludge / Sugarcane bagasse	127.00 %	(Jafari and Zilouei, 2016)

568

569   The outcomes of Table 2 in the view of production of bio–H_2 by means of NPs and
570   different lignocellulosic components mainly are depending on the kind of inter–activity
571   between the biomass material components and nano–catalyst. Further, the rate of electron
572   transfer improves the commercial bio–H_2 yield by making high availability of active surface
573   area with NPs for acceleration of reaction kinetics. Thereby, unwanted oxygen molecules can
574   be removed from the reaction mixture, simultaneously (Dey et al., 2022). Fe(iron)–NPs can
575   play as primary cofactor that can eventually be utilized for the production of bio–H_2 (73%) as
576   the main component for hydrogenase possibly was formed by such a nano system, since it has
577   been associated with the enzymes ferredoxin as well as hydrogenase of the electron transport
578   chain.   Some other significant nano system has been formed by Ag(silver), Au(gold),
579   Cu(copper), Pd(palladium), *etc*., to enhance production of bio–H_2 by means of dark
580   fermentation technique.

581

582   **4.   Research needs Perspectives and Future Directions**

583   The physical pretreatment methods lead to reduce the size of lignocellulosic biomass
584   components, cellulose crystalline index, and raise the availability of the catalytically active
585   sites. This method includes the application of either mechanical shredding *via* grinding
586   (milling and chipping), steam explosion, ammonia based pretreatments (AFEX) or radiation–
587   based techniques *via* ultrasonication, *γ*, electron beam and microwave radiations (Mankar et
588   al., 2021). In chemical pretreatment, the degradation/decomposition of lignocellulosic
589   biomass components in aquatic phase by means of chemical reactions *viz*. acidic hydrolysis,

alkaline hydrolysis, organo–solvent and inorganic salt *via* alkaline salt, metal salt, ionic liquid (IL) and deep eutectic solvent (DES) methods. The eco–friendly and energy efficient green bio–pretreatment processes include the microorganisms *viz*. bacterial, fungal and enzymes to selectively decompose/degrade hemicellulose and lignin moieties, consequently results in an enhanced enzymatic saccharification (Kumar et al., 2020). Though, the application of various kinds of chemical and physical pretreatments possesses their own issues in the bio–conversion of lignocellulosic biomass components. So, introduction of the physico–chemical pretreatment (combination of physical and chemical methods) processes is necessary for industrial applications. Further, these pretreatment processes enhance the solubility of hemicellulose and lignin content for destructuralization of lignocellulose moieties to improve the accessible specific surface on lignocellulosic biomass for enzymes, while with certain slight environmental impacts. The major physico–chemical pretreatment techniques consists of EA: Extractive ammonia and SAA: Soaking aqueous ammonia, supercritical fluid:SCF like $ScCO_2$: Supercritical carbon dioxide: ScH_2O: Supercritical water and $ScNH_3$: Supercritical ammonia explosion, liquid hot water :LHW, hydrothermolysis, uncatalyzed solvolysis, aquasolv and aqueous fraction processes, microwave assisted chemcial and SPORL a sulfite pretreatment: (Sulfite pretreatment to overcome recalcitrance of lignocellulose), hydrothermal (HT) explosion and wet air oxidation to overcome recalcitrance of lignocellulose processes (Akhtar et al., 2015; Kumari and Singh, 2018).

The exiting challenges in the case of bio–conversion of lignocellulose materials into fermentable sugar moieties and their consequent conversion into high value added bioenergy as well as by–products through various pretreatment approaches. Some of the pretreatment approaches have been utilized in large scale industrial stage, but till now some significant challenges fall in the category of intensively energy requirement, low process efficiency, generation of toxic or environmentally hazardous wastes/inhibitors, perturbation in the overall yield on fermentable sugar moieties, degradation of partial cellulose and lignocellulosic structure, *etc.* (Chauhan, 2020). Now, there is an emerging need for an environmental friendly technology that utilizes the solution of all above challenges *i.e.*, the need of green solvents, low consumption of energy and chemicals, minimization of the water usage, operation with reduced or small particle size, *etc.* The following factors are to be surely considered in order to make LCB (lignocellulose biomass) pretreatment processes efficient as well as effective, they are (i) utilization of large sized LCB particles to minimize the energy application, (ii) operation at very high concentrations of LCB materials to reduce

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623 the usage of water as well as energy sources and (iii) operation of integrated process to use

624 the excess heat or steam from other processes of the pretreatment steps. In most of the

625 chemical pretreatment process, the usage of catalysts (both acid, alkali or other chemicals),

626 which are easily miscible in water and the recovery of catalysts from waste water streams are

627 more energy intensive and expensive process *i.e.*, using phosphoric acid pretreatment process

628 results in the formation of very high digestible amorphous cellulose content, but the recovery

629 of acid from aqueous medium is more difficult and expensive process. Further, in some

630 pretreatment processes, the neutralization of chemicals by the additions of acid or base,

631 generate some salts or compounds which cause an additional cost for recovering and

632 recycling with water from consequent processing steps because another major challenges

633 (Janusz et al., 2020, 2017). The LCB pretreatment processes include mechanical processing,

634 microwave irradiation processing, wet oxidation, ozonolysis, hot water and supercritical CO_2

635 and H_2O techniques, no catalysts or expensive chemicals are utilized. So there is no recovery

636 of chemicals or compounds during the processing, but the above techniques need high

637 expensive reactor units (Balan, 2014). Till now, the challenge for the effective enzymatic

638 digestibility of LCB materials is unclear in biological pretreatment process, which is due to

639 the employed complicated structural unit present in the microbes or enzymes. Hence, each

640 pretreatment technology must be upgraded with effective reactor systems with capable of

641 performance at high solid concentrations with large particles and different variety of LCB

642 types and need low energy and water expensive process. So, the utilization of enzyme based

643 LCB pretreatment process overcomes the above challenges more efficiently and effectively

644 than the other technologies (Ponnusamy et al., 2019; Testa and Tummino, 2021).

645 Pretreatment steps for lignocellulosic biomass materials to fermentable sugars are a

646 challenge in the case of large–scale conversion for procuring cost–effective and competitive

647 technically derived products along with very low inhibitory concentration. Agricultural

648 residues have been utilized for industrial bio–fuel production *via* steam explosion, as it is an

649 important technology. This steam explosion in a 50 m³ industrial reactor with corn–stover

650 was performed, to yield 80% of hemicelluloses and then by hydrolysis more than 90 % of

651 celluloses were recovered (Kucharska et al., 2018). Pretreatment with dil. acids is

652 encouraging the production of bio–fuels, as of the biomass possesses high efficiency for the

653 conversion of most of the hemicelluloses into soluble sugars, whereas this process forms

654 furfural like inhibitors compounds. The efficacy of acid hydrolysis enhances the pretreatment

655 *via* optimization of reaction conditions and certain operational parameters *viz*. dosage of acid,

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pressure, time of retention, solid:liquid ratio and temperature. Silva et al., (Silva and Reis, 2016) studied three pretreatment techniques with dil. acids, liquid hot water and AFEX for the production of commercial bio–fuel. Techno–economic analysis has shown that the pretreatment process using LHW turned as a commercial one. The novel approach to lessen the technical issues with the performed pretreatment processes in a single operation, is concerned to combination of those processes *via* mechanical (crushing)–chemical, –electron beam– chemical (alkali), –microwave–chemical, –chemical–steam explosion and physical–biological processes (Chen et al., 2017). The combination of such techniques depends on kind of the biomass feed that integrates the advantage of the concern pretreatment technique. As well, in turn the combination of such processes can considerably progress the effectiveness of enzyme hydrolysis. Binod et al., (Binod et al., 2012) employed a combination of microwave–chemical (–acid and –alkali) pretreatment in place of conventional acid/alkaline pretreatment. The results reveal that the combined treatment enhances the fermentable sugar yield within a short period of time duration. Lai et al., (Lai and Idris, 2016) has suggested low–energy ultrasound–chemical (–alkali) pretreatment for the enhancement of biodegradable nature of lignocellulosic biomass feed. The combination of Ionic liquid–ultrasound process on bagasse, using cholinium IL is biocompatible, showing 80 % of the cellulose and 72% of hemicellulose saccharification along with a little inhibitory effect on enzyme cellulose activity (Ninomiya et al., 2015, 2012). The integration of bioprocesses for the industries to achieve coherent energy efficiency mainly involves the partly bioconversion of spent cooking oil into bio–fuels/cellulose products. Due to the overall cost of production on the lignocellulosic biomass biofuels by fermentation, the wastewater management has given to importance as the biorefinery stillage contains a range of dissolved and unutilized fermentable sugars mainly lignin of about 74.1–79.0 wt. % of the total biomass (Trinh et al., 2013). Consequently, this lignin has been utilized for the production of high–value added products/by direct combustion to supply sufficient energy for the industrial processes. In this regard, fast pyrolysis is currently attracting the interest of researchers since it has the potentiality for the efficient conversion of lignin to high commercially value products like as bio–oil, bio–char, *etc*. (Trinh et al., 2013). But for the production of gaseous bio–fuels towards the industrial application, a specific approach is required to comprehensively analyze the overall operating costs. The production of biogas by anaerobic digestion usually is a heat/energy generating integrated process. Thereby, integrated technologies for the production of bio–H_2 are taken into consideration because utilization of value added products

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and energy that can be cogenerated, simultaneously as the pretreatment techniques of lignocellulosic biomass is performed before the saccharification, enzymatically. In the case of bio–H$_2$, high cost and low yields along with comparatively low concentration of fermentation broth are still some major challenges.

The chemical pretreatment conventionally is utilizing acids and bases and it can be regarded as a cost–effective process. The by–products formed in this process should be purified and reused in the form of value–added products. Such kind of technique is commercially viable to treat the lignocellulosic biomass feed for bioconversion processes, while bio–fuels and other value added bio–products are derived. The recent familiar pretreatment techniques are generally energy–intensive. Thereby, the development on resourceful and cost–effective pretreatment processes is given significance in an industrial point of view. There, a popular industrial chemical pretreatment technique offers highly digestible biomass feed. Then, the recycling, recovery and utilization of liquids and solids productivity from the wastewater are also accessible, though those processes could be utilized and optimized mainly for bio–ethanol production (Kucharska et al., 2018). The pretreatment technologies for improving production of bio–H$_2$ from the DF process can be categorized according to their pretreated inoculums/substrates. They can be classified into physical, chemical, physico–chemical, biological and nano–technical pretreatments, based on the biomass used. Amongst, the dissimilar technologies reviewed, acid pretreatments are the mostly studied techniques for the substrates and inoculums. The most suitable emerging techniques over different studies, the hybrid/combined technologies have been given maximum yield. In addition, many pre–techniques have been employed for substrates pretreatment that may eventually form inhibitory compounds thereby can decrease bio–H$_2$ production. As a result, the research needs to find out the best technique for both the substrates and inoculums in industrial scale while a simultaneous consideration towards both energy consumption and technical feasibility in economic aspect. In the case of substrates, most studies have been focused on biomass residues from barley straw, corn stover, wheat straw, *etc*., food wastes, sludge, and wastewater stream to yield maximum. It has been concluded that among the various pretreatments investigated for such kind of wastes, ultrasound, combined and biological pretreatments have been utilized/employed to procure positive results.

5. Conclusions

Effective pretreatment technologies for improving production of bio–H_2 *via* fermentation from lignocellulosic biomass materials are highly desirable for both energy consumption and technical feasibility towards economic aspect. In addition, utilization of other value–added products *viz.* lignin derived molecules are highly recommended. This type of biorefinery approach is unavoidable for commercialization of lignocellulosic biomass materials.

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Graphical Abstract

136.
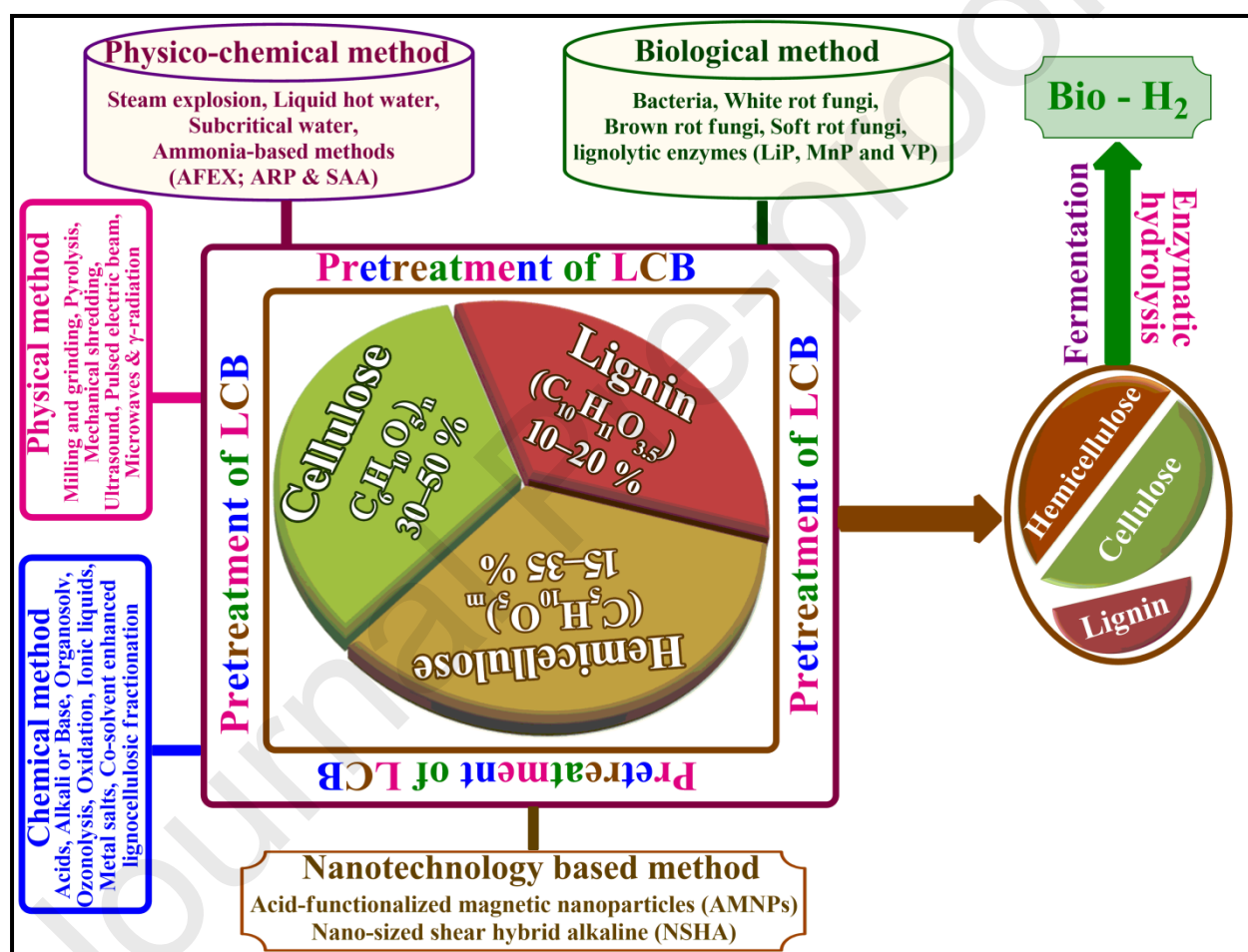
Highlights

- Recentlignocellulosic pretreatments have been documented.
- Radiation energy based pretreatment techniques were discussed.
- Role of nanotechnology in bio–H_2 production has been highlighted
- Challenges in the development of pretreatments and remedies are suggested.

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CRediT authorship contribution statement

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1239 Writing – review & editing. Retnam Krishna Priya: Writing – review & editing. Rajesh Banu
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1241 Writing – review & editing, Rijuta Saratlae– Writing – review & editing, Gopalakrishnan
1242 Kumar: Writing – review & editing, Funding acquisition, Project administration &
1243 Supervision.

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1245   138.