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Review article

Application of nanoparticles in biofuels: An overview

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ABSTRACT

Biofuels are fast advancing as alternative sources of renewable energy due to their non-polluting features and cost-competitiveness in comparison to fossil fuels. However, in order to fast-track their development, focus is shifting towards the use of technologies that will maximize their yields. Nanoparticles are gaining increasing interest amongst researchers due to their exquisite properties, which enable them to be applied in diverse fields such as agriculture, electronics, pharmaceuticals and food industry. They are also being explored in biofuels in order to improve the performance of these bioprocesses. This review critically examines the various studies in literature that have explored nanoparticles in biofuel processes such as biohydrogen, biogas, biodiesel and bioethanol production, towards enhancing their process yields. Furthermore, it elucidates the different types of nanomaterials (metallic, nanofibers and nanotubes) that have been used in these bioprocesses. It also evaluates the effects of immobilized nanoparticles on biofuels such as biodiesel, and the ability of nanoparticles to effectively suppress inhibitory compounds under certain conditions. A short section is included to discuss the factors that influence the performance of nanoparticles on biofuels production processes. Finally, the review concludes with suggestions on improvements and possible further research aspects of these bioprocesses using nanoparticles.

1. Introduction

The depletion of hydrocarbon fuel reserves, the increase in environmental pollution, and unstable energy prices have triggered a search for clean and sustainable energy resources [1–5]. Biofuel development initiatives are widely being implemented in many countries in order to mitigate these challenges [6–9]. They are classified into two groups i.e. primary and secondary biofuels. The primary biofuels are directly produced from plants, forests, animal waste and crop residues [10–12]. Secondary biofuels are produced from a combination of biomass feedstocks and microorganisms, and are further categorized into three groups i.e. first generation, second generation, and third generation biofuels [13,14]. First generation biofuels are generated from edible crops such as corn, wheat, sugarcane, barley, sorghum, sunflower oil, etc. Second generation biofuels are synthesized from biomass residues such as wheat straw, grass, jatropha, miscanthus, cassava, corn cob, etc [15–17]. These biofuels are considered a viable option because they do not a pose a threat to food security, deforestation, water shortages, and other social challenges [18,19]. Meanwhile, the third generation biofuels use various types of microalgal species [15,20]. Over the last decade, research focusing on third generation biofuels has also intensified because microalgae can thrive under diverse growth conditions and can produce different types of renewable fuels such as biohydrogen, biodiesel, and biogas [21,22].

Biofuels such as biohydrogen, biodiesel, bioethanol and biogas are receiving increasing attention amongst researchers because they are environmentally friendly, use diverse feedstocks that are accessible, non-edible and cheap [23–25]. Biohydrogen is gaining increasing prominence over contending biofuel technologies due to its characteristics which include: (i) high energy content (120 kJ/g) that is approximately 3 times greater than that of fossil fuels i.e. sub-bituminous coal (25–35 kJ/g), gasoline (41.2 kJ/g), and diesel (42.9 kJ/g), (ii) its carbon-sequestration abilities, (iii) its ability to utilize diverse feedstocks including organic effluents, (iv) its ability to use diverse bacteria which are found in various environments, (v) it can be produced at ambient temperature and pressure, thus making it feasible for its large-scale production, and (vi) the process offers the simplest way of producing hydrogen energy [26]. The process is highly dependent on various operational conditions such as substrate concentration, pH, temperature and hydraulic retention time [26]. Therefore, these

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Nomenclature

Abbreviations

BBD	box behnken design
CCD	central composite design
COD	chemical oxygen demand
DFE	dark fermentation effluents
DNA	deoxyribonucleic acid
Fe^0	zero-valent iron
PCR	polymerase chain reaction
TEM	transmission electron microscopy
TVS	total volatile solids
VFAs	volatile fatty acids
VS	volatile solids
VSS	volatile suspended solids
ZVI	zero-valent iron

Units

d	day
g	gram
h	hour
kJ	kilojoule
mg	milligram
Kg	kilogram
L	liter
mL	milliliter
mol	mol amount
nm	nanometer
t	time
USD	united states dollar

parameters must be optimally controlled in order to maximize the biohydrogen yields [26]. Moreover, this technology can be used as a component in biorefinery processes for enhanced energy recovery. For instance, dark fermentative biohydrogen production is used as the initial process, the resulting dark fermentation effluents (DFE) which consists of volatile fatty acids and alcohols are then used in secondary fermentation processes such as biomethane, bioelectricity, photo-fermentation, resulting in high energy recovery [27,28]. In addition, the soluble by-products in DFE can further be converted to other value-added chemicals such as ethanol, propanol and butanol [29,30].

Meanwhile, biogas has contributed immensely in the evolution of biofuels due to its widespread acceptance and sustainability [31–33]. Besides its application as an alternative fuel, it is used in waste management approaches [34]. Biogas is generated through a biochemical process known as anaerobic digestion, which is facilitated by various groups of archaeal and bacterial species. These organisms are found in many environments such as wastewaters, landfills, composts and animal farms [35,36]. Furthermore, this process is conducted under various operational conditions of substrate concentration, pH, temperature, organic loading rate and hydraulic retention time [36]. Biogas comprises mainly of 50–75% methane (CH_4), followed by 25–45% carbon dioxide (CO_2), and small traces of other components such as hydrogen sulfide (H_2S) [37]. The process of anaerobic digestion is extensively used in many countries, including Brazil, China, United States, United Kingdom, Netherlands, and Germany [38]. In Europe alone, a large number of anaerobic digesters have been built at various agricultural sites for the treatment of manure and other organic residues [38]. This has significantly increased the continent's biogas market i.e. more than 14.9 million tons of biogas was produced in 2014 [39]. Germany is the current leader in biogas technology and thus plays a pivotal role in biogas market in Europe. Between the year 2000 and 2014, the number of biogas facilities in Germany increased from 1050 to 7850 [40].

Biodiesel is another clean energy that is considered a suitable substitute for petroleum diesel, due to its environmental friendliness and the fact that it can be produced using non-edible oils [41–44]. The biodiesel industry has been experiencing significant growth in recent years i.e. the global biodiesel industry is expected to expand with an annual increase of 7.3%, to a total of 54.8 billion USD by 2025 [45]. Other biofuel options such as bioethanol and biomethane have also been proposed by scientists and other stakeholders as probable candidates that can be used to intensify the renewable energy markets [46,47]. Bioethanol is also foreseen as an alternative fuel that can be used to address the pressing energy demands as well as environmental concerns [48,49]. The production of bioethanol started in the early 1900s in the United States and Europe, and is estimated to have an annual growth of 3–7% [12]. Furthermore, the global ethanol production was estimated at around 100 billion litres in 2017, and is envisaged to double in the next decade [12]. The production of second generation bioethanol is not yet developed, compared to first generation bioethanol. Nonetheless, the challenges associated with first generation biofuels has reinvigorated scientists and other stakeholders to look for alternative methods of producing biofuels. Therefore, bioethanol derived from lignocellulosic feedstocks has enormous potential to strengthen its global production [50]. These feedstocks do not pose any socio-economic concerns because they are cheap, abundant and considered waste [51]. Furthermore, the global production of plant biomass is estimated at 200 billion tons/year, of which 90% are lignocellulosic wastes [52]. This highlights their potential towards the intensification of renewable fuels.

In spite of many scientific breakthroughs, second generation biofuels are still hindered by various technical barriers that must be overcome before they can compete with fossil fuels [53]. For example, pretreatment methods needs to be applied to lignocellulosic biomass in order to extract the fermentable sugars before they can be used in biofuel processes [54]. These pretreatment methods are often expensive and escalate the production costs [55]. Secondly, biofuels are plagued by low yields due to the formation of inhibitory compounds, which prevent metabolic processes [56,57]. Fermentation inhibitors such as furan derivatives, aliphatic compounds, phenolic compounds and inorganic ions are formed during the pretreatment of lignocellulosic biomass and thus reduce the biofuel yields [58]. In addition, it has been shown in literature that the fermentation processes are accompanied by side-reactions which lowers the yield of the desired product [59]. This is common in biofuels such as biohydrogen production, whereby various inhibitors such as H_2-consuming bacteria i.e. hydrogenotrophic methanogens, homoacetogens, sulfate-reducing bacteria, nitrate-reducing bacteria and volatile fatty acids (acetic acid, butyric acid, propionic acid, etc.) are formed during the acidogenic-solventogenic stage, resulting in low biohydrogen yields [60,61]. These barriers necessitates the development of novel optimization strategies that can be used to achieve high process yields, and pave a way for the establishment of a viable biofuel industry that can compete with fossil fuels.

The field of nanotechnology has intensified over the past few decades due to its ability to use diverse nanoscale materials, having sizes in the range of 1–100 nm [59–62]. As a consequence, nanoparticles are employed in various applications such as the agricultural, food, cosmetic, pharmaceutical, and electronic industry [59–62]. The use of nanotechnology in these different fields is mainly attributed to the novel properties of nanoparticles which include their nanoscale size, structure/morphology and high reactivity [59–62]. The extremely small size of nanoparticles allows: (i) for a large surface-area-to-volume-ratio and causes an increased number of active sites which are essential for producing different reactions and processes, (ii) the ability of nanoparticles to exhibit different morphologies has also widened their applications in many fields such as drug delivery, bioimaging, water treatment/environmental remediation, etc, and (iii) nanoscale materials react at a faster rate with other molecules, compared to large particles [66,67]. Furthermore, nanoparticles exhibit other favorable characteristics such as a high degree of crystallinity, catalytic activity, chemical stability and high adsorption capacity [64]. They can either be metallic, semiconductor or polymeric in nature, and are synthesized using a top-down or bottom-up approach [67,68].

These unique properties have made nanoparticles to be attractive materials for enhanced biofuel processes. They are mostly used as catalytic agents and play an important role in the transfer of electrons, reduce inhibitory compounds, and improve the activity of anaerobic consortia [63–71]. The use of nanoparticles in biofuels is still in its infancy. Therefore, there are few reviews that focuses on this topic. This paper presents for the first time, a review that discusses nanoparticles as catalysts in biofuel processes of biohydrogen, biogas, biodiesel and bioethanol production. Furthermore, it elucidates the different types of nano-additives (metallic, nanofibers and nanotubes) that are used in these bioprocesses, in an attempt to enhance their process yields. Finally, the review provides suggestions on improvement of biofuel production processes using nano-based materials.

2. Application of nanoparticles in biofuel production processes

The use of nanoparticles is gaining increasing momentum in biofuel production processes due to their enhancement effects on metabolic reactions of these bioprocesses as highlighted earlier. Various nanomaterials such as nanofibers, nanotubes and metallic nanoparticles have been reported in biofuel production processes [72,73]. This section reviews studies that have used nano-scale materials as catalysts in an attempt to improve the biofuel production performance/yields. In the context of this review, the types of biofuels that will be considered are biohydrogen, biogas, biodiesel and bioethanol.

2.1. Biohydrogen production

Biohydrogen production is carried out by a diverse group of anaerobic bacteria which use various metabolic routes to generate molecular hydrogen [26]. The process is highly dependent on operational conditions such as substrate concentration, pH, temperature and hydraulic retention time which must be optimally controlled in order to maximize its yield as highlighted [74,75]. These parameters are important because they stimulate the activity of biohydrogen-producing bacteria [26]. It has also been shown that the activity of microorganisms can be enhanced by using nanoparticles in anaerobic conditions because they increase the transfer of electrons in metabolic processes [76–79]. They also improve the kinetics of biohydrogen-producing processes due to their ability to react faster with electron donors [67,77].

2.1.1. Dark fermentative biohydrogen production

Dark fermentative biohydrogen production provides a cost-effective and environmentally friendly process because it can be produced under mild fermentation conditions using different renewable feedstocks and microorganisms which are found in many environments [26]. Several nanoparticles have been shown to improve the performance of dark fermentation process. For example, Zhang and Shen [78] showed that the incorporation of 5 nm gold nanoparticles improved the substrate utilization efficiency by 56% during dark fermentation. The nanoparticles also increased the biohydrogen yield by 46% [78]. Gold nanoparticles has a stimulatory effects on biohydrogen-producing processes because they provide a large surface-area-to-volume-ratio for bacteria to bind in active sites of molecules. They also enhance the microbial processes i.e. the activity of biohydrogen-producing enzymes such as [Fe-Fe]- and [Ni-Fe]-hydrogenases and ferredoxins (proteins that mediate the transfer of electrons in biohydrogen-producers) is improved as a result of these nano-based additives [72,73].

Nanoparticles of other elements have been used in the enrichment of dark fermentative biohydrogen-producing bacteria [80,81]. However, they must be used at optimum concentrations because they inhibit the growth of microorganisms at high concentrations. The effects of silver nanoparticles on dark fermentative biohydrogen production process was investigated by Zhao et al. [80] in anaerobic batch reactors. It was observed that the addition of silver nanoparticles (20 nmol/L) enhanced the glucose conversion by 62%, which led to a maximum biohydrogen yield of 2.48 mol H_2/mol glucose. These nanoparticles were beneficial to biohydrogen-producers because they reduced the lag phase and favored the acetic reaction, which is the main biohydrogen-producing pathway. They were also instrumental in maintaining the acidogenic phase i.e. pH was maintained at 5–7 throughout the process.

In an effort to understand the mechanism and microbial community dynamics of using zero-valent iron (Fe^0) nanoparticles, Yang and Wang [81] conducted a dark fermentative biohydrogen process using grass at mesophilic conditions (37 °C). It was shown that the use of Fe^0 nanoparticles favored the activity of predominant biohydrogen-producers. Moreover, microbial analysis showed a change in bacterial composition from *Enterobacter* sp. to *Clostridium* sp., which implies that the Fe^0 nanoparticles induced a more efficient biohydrogen-producing pathway that promoted the activity of the main biohydrogen-producers such as *Clostridium* species [81]. It was also concluded that the Fe^0 nanoparticles might have stimulated the activity of hydrogenases (enzymes that promotes the production of biohydrogen), resulting in a maximum biohydrogen yield and production rate of 64.7 mL/g dry grass and 12.1 mL/h. These values were 73.1% and 128.3% higher than that of the control experiments. Other studies investigated the use of predictive models such as central composite design (CCD) and box-behnken design (BBD), which are statistical-based tools that are used in the analysis and optimization of biotechnological processes [76]. These multivariate models are used to assess the linear and interactive effects of operational conditions on bioprocess yields [76]. These tools have also been used to acquire deeper insights into the optimum range of nanoparticles used in dark fermentation processes. Mullai et al. [82] studied the effect of initial pH, glucose concentration and nickel nanoparticle concentration on dark fermentation process using CCD. The nanoparticle size of 13.64 nm was effective in maximizing the biohydrogen yield. Consequently, a maximum yield of 2.54 mol H_2/mol glucose was obtained at glucose concentration of 14.01 g/L, initial pH of 5.6 and nickel concentration of 5.67 mg/L, respectively. Similarly, Vi et al. [83] used BBD in the optimization of dark fermentative biohydrogen-producing setpoint conditions of substrate concentration, pH and iron nanoparticle concentration at mesophilic conditions (30 °C). This resulted in a cumulative biohydrogen yield of 3501 mg/L which was achieved at optimized conditions of 27.63 g/L, 6.05 and 63.17 mg/L, for substrate concentration, pH and $FeSO_4$ nanoparticle concentration, respectively. The use of iron was also advantageous in this study because it acts as a co-factor in active sites of hydrogenase enzymes which in turn maximizes the activity of biohydrogen-producers [77]. It can therefore be concluded from these results that statistical-based tools along with nanoparticles can play an important role towards the enhancement of biohydrogen production yields, and also help to overcome some of the process barriers such as low yields, low substrate conversion and fermentation inhibitors, which prevents the scalability of biohydrogen production processes.

Metallic nanoparticles are gaining increasing prominence in the scientific fraternity owing to the fact that these materials can be synthesized using various functional groups which increases their stability and enables them to be conjugated with ligands, antibodies and drugs, thus widening their application in fields such as diagnostic imaging, biotechnology, drug delivery and magnetic separation [84–86]. These nano-based additives are also used in dark fermentative biohydrogen enhancement approaches. For example, Beckers et al. [87] examined the role of three metallic nanoparticles (Pb, Ag and Cu) along with FeO nanoparticles in biohydrogen production using *Clostridium butyricum*. These metallic nanoparticles were immobilized on porous silica (SiO_2) at low concentration of 10^{-6} mol/L. The microorganisms that were encapsulated in FeO nanoparticles increased the biohydrogen yield and biohydrogen production rate by 38% and 58%, respectively, compared with the cultures without FeO nanoparticles. This was due to an improvement in hydrogenase activity and transfer of electrons which occurred during dark fermentation process. In another study, Elreedy et al. [88] studied the effects of Ni nanoparticles and Ni-graphene nanocomposite on dark fermentative biohydrogen production using industrial wastewater. Maximum biohydrogen production yields of 24.73 ± 1.12 mL H_2/g $COD_{initial}$ and 41.28 ± 1.69 mL H_2/g $COD_{initial}$, were obtained using Ni and Ni-graphene nanoparticles, respectively, at nanoparticle concentration of 60 mg/L. However, it was shown that a further increase in nanoparticles concentration decreased the biohydrogen yield, due to antimicrobial properties (inhibition of biohydrogen-producing pathways), as highlighted in similar studies.

There has been a rapid growth in the exploitation of mesoporous silica nanoparticles due to their porous and morphological features which also broadens their application in fields such as bioimaging, drug/gene delivery and food industry [89–91]. These nanocarriers can be synthesized using various methods including cost-effective and non-toxic processes. The morphology, pore size and particle size of mesoporous silica nanoparticles can be modified by controlling the reaction conditions such as pH, temperature, surfactants concentration, and silica source [92,93]. Amongst the mesoporous silicas, Santa Barbara Amorphous (SBA-15) is a material with outstanding properties such as high surface-area-to-volume-ratio, high thermal stability, uniform pores and thick framework walls [94–96]. These unique features have made SB-15 an attractive material that can be used for the enhancement of biohydrogen-producing biochemical pathways. Venkata Mohan et al. [97] showed that SBA-15 silica nanoparticles (120 mg/L) can increase the production of biohydrogen by 544% (7.02 mol/kg COD.d) compared with the control (1.09 mol/kg COD.d) at high loading rate of 2.55 kg COD/m^3.d. The silica nanoparticles also produced a biohydrogen yield (7.02 mol/kg COD.d) that was 347% higher than that of the activated carbon nanoparticles (1.57 mol/kg COD.d). Furthermore, novel methods have been incorporated in silica nanoparticles in order to enhance their performance and recovery in dark fermentation processes. Therefore, iron oxide (Fe_3O_4) nanoparticles are conjugated to silica (SiO_2) nanoparticles via amide bond to produce Fe_3O_4@SiO_2

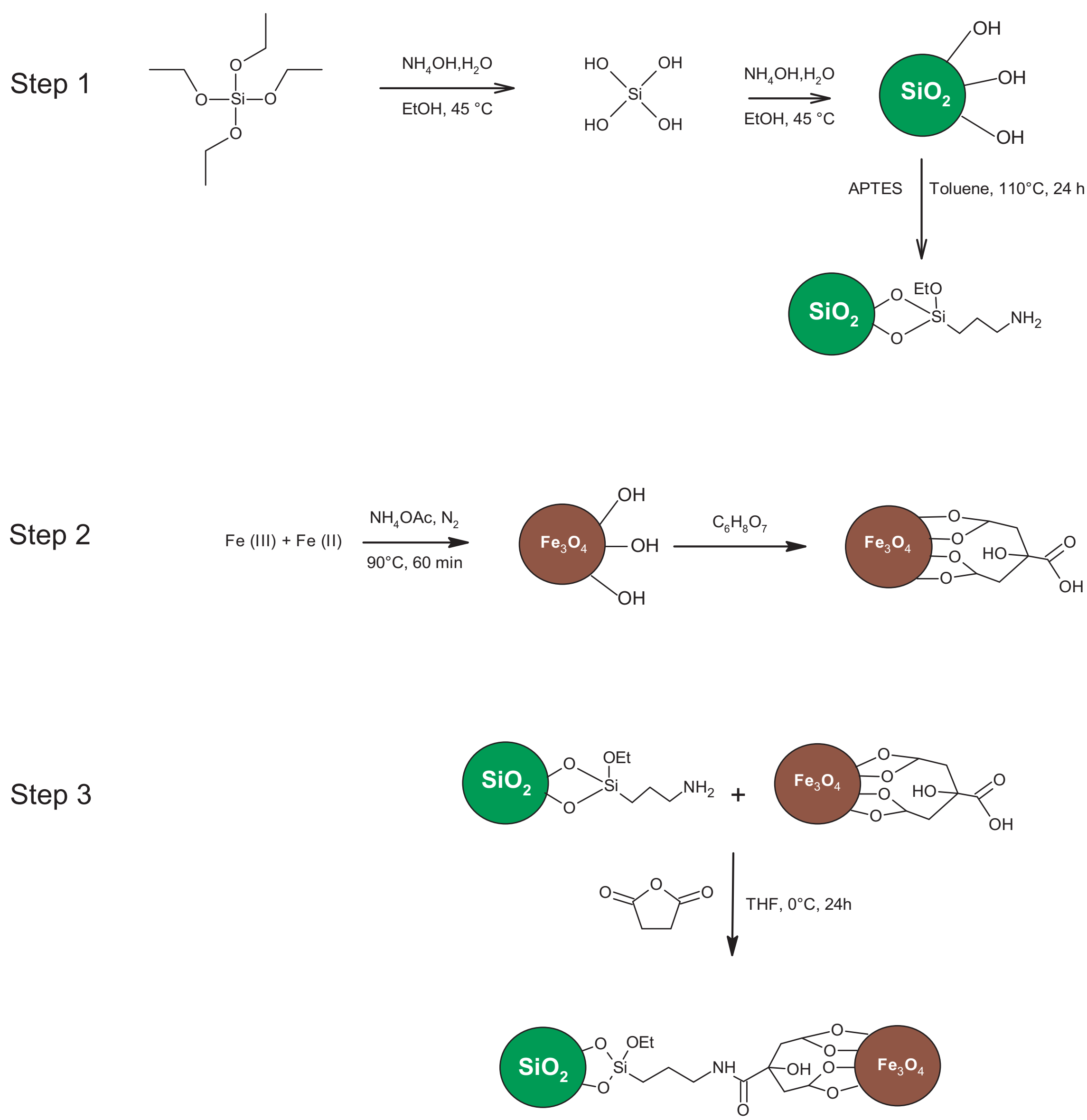

Fig. 1. Synthesis of the Fe_3O_4@SiO_2 nanoparticle conjugate [100].

nanoparticles. The newly synthesized $Fe_3O_4@SiO_2$ nanoparticles are advantageous in dark fermentation because they are more stable, have a high catalytic performance and can be recovered after the fermentation process [97]. $Fe_3O_4@SiO_2$ nanoparticles also have a high thermal stability, high hydrophilicity, low toxicity and can function in a broader pH range [98,99].

In order to gain some insights into the synthesis of $Fe_3O_4@SiO_2$ nanoparticles, a detailed procedure for the production of these nanoparticles is shown in Fig. 1. Step 1 illustrates the synthesis of silica nanoparticles via the Stöber method and further functionalization using (3-aminopropyl) triethoxysilane (APTES) to produce amine-functionalized silica nanoparticles [100,101]. In step 2, iron salts (e.g. $FeCl_3$ and $FeCl_2$) are used as precursors for synthesis of Fe_3O_4 nanoparticles using the co-precipitation method [102,103]. The Fe_3O_4 nanoparticles can be stabilized using citric acid, which contains the carboxyl groups (-COOH) that are essential in the conjugation of Fe_3O_4 nanoparticles with the amine-functionalized silica nanoparticles, as shown in step 3 [104]. This conjugation between SiO_2 and Fe_3O_4 nanoparticles can be confirmed by amide-bond formation using Fourier Transform Infrared Spectroscopy (FTIR) [105].

Other dark fermentation studies examined the effects of nanoparticles on biohydrogen yields using genetically modified bacterial strains. Mohanraj et al. [106] investigated the effect of Cu and $CuSO_4$ nanoparticles on biohydrogen production using *Clostridium acetobutylicum* NCIM 2337 and *Enterobacter cloacae* 811101. It was observed that the addition of Cu and $CuSO_4$ nanoparticles had a negative effect on the production of volatile fatty acids (VFAs), which led to the inhibition of acetate and butyrate biohydrogen-producing pathways [87].

On the other hand, Nath et al. [107] demonstrated that the supplementation of iron nanoparticles had a significant increase on biohydrogen yield, compared with the control experiment. This led to an enhanced biohydrogen yield of 1.9 mol H_2/mol glucose, which was achieved at iron concentration of 100 mg/L. The nanoparticles increased the utilization of glucose by two-fold. These results correlate with literature because iron is an important component of ferredoxin and also acts as an electron carrier in hydrogenase enzymes [107]. Dolly et al. [108] evaluated the influence of iron nanoparticles on biohydrogen production process using mixed co-cultures of *Rhodobacter sphaeroides* NMBL02 and *Escherichia coli* NMBL04. The addition of iron nanoparticles increased the biohydrogen yield by 20%. The authors also conducted a parametric optimization study using BBD in order to determine the optimum pH, malate concentration and iron concentration. The model predicted the optimum process conditions of 5.6, 3.948 g/L and 312.168 mg/L for pH, malate concentration and iron concentration, respectively. This resulted in a high biohydrogen yield of 2046 mL H_2/L of medium. In another study, TiO_2 and Fe nanoparticles were shown to have a stimulatory effect on *Clostridium pasteurianum* [109]. The addition of 50 ppm nanoparticles generated a high biohydrogen production rate of 8.7 H_2 L/L.d. Although there was an enhancement in biohydrogen production, it was observed that this improvement did not occur at the gene level, but was caused by the increased flow of electrons during the fermentation process [109].

Lin et al. [110] maximized the biohydrogen yield by adding Fe_2O_3 nanoparticles in dark fermentative biohydrogen production involving pure cultures of *Enterobacter aerogenes* ATCC13408 in a starch medium. The biohydrogen yield was increased from 164.5 ± 2.29 mL H_2/g starch to 192.4 ± 1.14 mL H_2/g starch, when the nanoparticles concentration was varied from 0 to 200 mg/L. Transmission electron microscopy (TEM) images showed cellular internalization of Fe_2O_3 nanoparticles, which indicated that the activity of [Fe-Fe]- and [Ni-Fe]-hydrogenase was enhanced due to the release of Fe molecules.

2.1.2. Photo fermentative biohydrogen production

Nanoparticles have also been used to improve the activity of photosynthetic biohydrogen-producing microorganisms such as microalgae. Studies that evaluated the application of nanoparticles in algal biotechnology showed that these materials increase biomass growth and physiological processes such as photosynthetic activity, nitrogen metabolism, and protein level in microalgal species [67]. They serve as catalytic agents and induce metabolic pathways which promotes the synthesis of photosynthetic pigments (chlorophyll *a*, chlorophyll *b*, carotenoids, anthocyanin, etc), lipid production and nitrogen metabolism [111,112]. They also favor the production of carbohydrates, which in turn promotes the growth of algal cells [113,114]. Furthermore, nanoparticles boost the activity of the key enzymes such as glutamate dehydrogenase, glutamate-pyruvate transaminase, glutamine synthase and nitrate reductase, and these enzymes are essential for the metabolism of microalgal species [115,116].

Several nanoparticles have been assessed in photosynthetic biohydrogen-producing processes. The photosynthetic activity of *Chlorella vulgaris* was maximized by adding optimum concentrations of silver nanoparticles and gold nanorods in batch processes [67]. Moreover, it was observed that zero-valent iron (Fe^0) nanoparticles increased the growth of microalgal species due to an increase in the formation of chlorophyll and carotenoid pigments [67]. This phenomenon was also documented in other photo fermentation studies. For instance, zero-valent iron (Fe^0) shavings were used to maximize the biohydrogen yield in a sucrose medium [117]. An optimum biohydrogen yield of 4.2 mol H_2/mol sucrose was achieved at Fe^0 concentration of 8–16 g/L. This yield was two times higher than that of the control experiment [92]. TiO_2 nanoparticles were also used to produce a maximum biohydrogen production rate of 1990 mL H_2/L using photosynthetic bacterium *Rhodobacter sphaeroides* NMBL02 [118]. The rate of biohydrogen was enhanced by 50% in the presence of 60 µg/mL TiO_2 nanoparticles. There is no clear mechanism that has been established in literature regarding the role of nanoparticles in biohydrogen-producing microorganisms. A plausible explanation to higher biohydrogen yields may be due to the ability of nanoparticles to maintain the pH of the medium, which also stimulates the activity of hydrogenase enzymes and substrate hydrolysis [118,119]. The addition of nanoparticles also enhance the biohydrogen-producing metabolic pathways such as acetate and butyrate reactions [118,120]. It has also been shown that zero-valent (Fe^0) nanoparticles increase the activity of biohydrogen-producers by being transformed into ferrous iron (Fe^{2+}) during the fermentation process (Eq. (1)) [121]. Besides, Fe^0 nanoparticles improves the activity of major enzyme related to hydrolysis and acidification during the biohydrogen production process [121,122].

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2 \tag{1}$$

Silica nanoparticles were also used to enhance the photo fermentation efficiency of *Chlamydomonas reinhardtii* CC124 in a compact tubular photobioreactor [123]. The addition of nanoparticles caused a significant increase in microalgal growth i.e. algal growth was measured as chlorophyll concentration (79.5 mg/L). The silica nanoparticles were used to scatter light within the reactor. This promoted the growth of microalgal cells because there was uniform distribution of light during the photosynthetic process. These nanoparticles also produced a cumulative biohydrogen production of 3121.5 ± 178.9 mL and a 23% increase in the final chlorophyll concentration [123]. Nanomaterials such as nanofibers are also reported in biohydrogen production processes due to their excellent properties such as large surface-area-to-volume-ratio, high porosity, small pore size and a diameter range of 50–100 nm [124].

2.1.3. Photocatalytic hydrogen production

Photocatalytic hydrogen production involves the splitting of water molecules into H_2 and O_2 in the presence of a photocatalyst using an illuminating source [125]. Various semiconductor, nano-based materials have been used in photocatalytic hydrogen production [126,127]. Amongst the studied photocatalysts, titanium dioxide (TiO_2) is reported to be the most favorable photocatalyst due to its non-toxic properties, chemical stability, low cost and high photocatalytic performance

[128,129]. Hakamizadeh et al. [130] synthesized mesoporous TiO_2/activated carbon, Pt/TiO_2, and Pt/TiO_2 activated nanocomposites via the sol–gel method. The authors also investigated the photocatalytic efficiency of these nanomaterials under ultraviolet light. The results showed that Pt/TiO_2/activated carbon nanocomposites are the most suitable photocatalysts, and generated a high hydrogen production rate of 7490 μmol/h/g photocatalyst, which was approximately 75 times higher than that of the conventional P25 (Aeroxide TiO_2 P25) photocatalyst [130,131]. Photocatalytic materials such as cadmium sulfide nanofibers were also reported for hydrogen production [132]. The cadmium sulfide nanofibers were synthesized using the precipitation method and were integrated with chemicals such as ethylenediamine (EN), butanol, acetonitrile and tetrahydrofuran. These nanofibers were also assessed for photocatalytic hydrogen production under blue-light irradiation. It was concluded that the photocatalytic efficiency was highly dependent on the presence of EN, on the nanofiber surface. The EN along with the cadmium ions assisted in creating the surface states. The blue-light photogenerated electrons from the semiconductor, which were stored in the surface states, were then transferred to the protons to generate hydrogen. Other materials such as TiO_2-graphene nanocomposites were also analyzed for photocatalytic performance of hydrogen evolution from water splitting [133]. It was observed that TiO_2-graphene nanocomposites possessed higher light absorption and charge separation efficiency than TiO_2 nanocomposites alone. Overall, these account of literature demonstrate the potential of nano-based additives towards the advancement of biohydrogen production technologies. The different nanoparticles that have been used to enhance the biohydrogen production yield are summarized in Table 1.

2.2. Biogas production

Anaerobic digestion is a biochemical process that converts various organic materials into biogas and its constituents (alcohols and VFAs) [143,144]. The process consists of four important steps i.e. hydrolysis, acidogenesis, acetogenesis and methanogenesis [145–147]. In the first step, large molecules (carbohydrates, proteins and lipids) are converted into monomers (soluble sugars, amino acids and VFAs) using various pretreatment methods (biological or physical). These monomers are metabolized by acidogenic (fermentative) bacteria in the second step to produce hydrogen, carbon dioxide, VFAs and alcohols, through a series of biochemical pathways [148,149]. In the third step, acetogenic bacteria use the soluble intermediates from the acidogenic process to produce hydrogen, carbon dioxide and acetic acid [150–152]. The proliferation of these bacterial species along with the acidogens requires a low partial pressure. The final stage is the methanogenesis process, whereby acetic acid, hydrogen and carbon dioxide are used by acetoclastic and hydrogenotrophic methanogens to generate methane. The main requirement for the growth of methanogens is also the maintenance of low hydrogen concentration [150–152].

The supplementation of nanoparticles has shown promising results in anaerobic processes, particularly in relation to electron donors/acceptors and cofactor of key enzymes such as [Fe]- and [Ni-Fe]- hydrogenase [143,153–155]. The use of nanoparticles increases the hydrolysis of organic matter. The increase in substrate conversion (hydrolysis) might be due to the fact that the nanoparticles provide a large surface-area-to-volume-ratio for microorganisms to bind in active sites of molecules, which in turn stimulates their biochemical processes (the activity of hydrogenase enzymes and ferredoxins), as highlighted in previous studies [108–113]. Nanoparticles of various materials have been reported in anaerobic digestion processes (Table 2). These include zero-valent metals, metal oxides and carbon-based nanomaterials [143,156,157].

Su et al. [158] studied the effects of zero-valent iron (ZVI) nanoparticles on biogas production using waste activated sludge at mesophilic conditions (37 °C). The addition of 0.1 wt% ZVI nanoparticles enhanced the concentration of methane in biogas by 5.1–13.2% and improved the biogas production rate by 30.4%. The use of ZVI nanoparticles was also effective in the removal of impurities such as hydrogen sulfide (H_2S). Consequently, the concentration of H_2S was reduced by 98% [158]. Moreover, Karri et al. [159] examined the role of ZVI nanoparticles as an electron donor during sulfate removal in mixed anaerobic sludge. The production of methane increased while the sulfate was significantly reduced. Hence, the highest methane formation rate (0.310 mmol CH_4 formed/mol Fe^0.d) and sulfate reduction rate (0.804 mmol SO_4^{2-} reduced/mol Fe^0.d) was obtained using the finest grade (0.01 mm) of ZVI nanoparticles. The presence of impurities (H_2S, CO, NH_3, etc) in biogas poses many challenges because they are corrosive to equipments (e.g. gas pipelines and combustion engines) and harmful to humans [160–162]. They also reduce the density and

Table 1
Types of nanoparticles reported in biohydrogen production studies.

Nanoparticle type	Microorganism	Feedstock	H_2 yield/rate	H_2 yield increase (%)	Refs.
Au	*Clostridium butyricum*	Artificial wastewater	4.48 mol H_2/mol sucrose	61.7	[78]
Ag	*Clostridium butyricum*	Inorganic salts	2.48 mol H_2/mol glucose	67.5	[80]
Ni	Granular sludge	Inorganic salts	2.54 mol H_2/mol glucose	22.71	[82]
$FeSO_4$	Anaerobic sludge	Potato starch	3501 mL H_2	–	[83]
Pd, Ag, Cu, Fe_xO_y	*Clostridium butyricum*	Growth medium	2.2 mol H_2/mol glucose	38	[87]
Ni-Gr	Mixed culture	Synthetic wastewater	41.28 mL H_2/g COD	105	[88]
Cu	*Clostridium acetobutylicum*	Glucose	1.74 mol H_2/mol glucose	–	[106]
Cu	*Enterobacter cloacae*	Glucose	1.44 mol H_2/mol glucose	–	[106]
Fe	*Enterobacter cloacae*	Inorganic salts	1.9 mol H_2/mol glucose	68.4	[107]
Fe	*Rhodobacter sphaeroides* + *Escherichia coli*	Growth medium	3.1 mol H_2/mol malate	–	[108]
Fe_2O_3	*Enterobacter aerogenes*	Cassava starch	192.4 mL H_2/g cassava starch	17.0	[110]
TiO_2	*Rhodobacter sphaeroides*	Sistrom's medium	1900 mL H_2/L	53.9	[118]
Si	*Chlamydomonas reinhardtii*	Tris acetate phosphate	3121.5 mL H_2	–	[123]
Au	Anaerobic sludge	Inorganic salts	105 mL H_2/L.d	–	[134]
Fe_2O_3	Mixed culture	Distillery wastewater	44.28 mL H_2/g COD	–	[135]
Fe_2O_3	*Clostridium acetobutylicum*	Growth medium	2.33 mol H_2/mol glucose	52	[136]
FeO	Mixed culture	Growth medium	1.92 mol H_2/mol glucose	7.9	[137]
Fe, Ni	Anaerobic sludge	Growth medium	149.6 mL H_2/g VS	200	[138]
α-Fe_2O_3	Mixed culture	Inorganic salts	3.57 mol H_2/mol sucrose	32.64	[139]
γ-Fe_2O_3	Starch wastewater	Mixed culture	104.75 mL H_2/g COD	–	[140]
γ-Fe_2O_3	Sugarcane bagasse	Anaerobic sludge	0.874 mol H_2/mol glucose	62.1	[141]
TiO_2	*Rhodopseudomonas palustris*	Growth medium	–	46.1	[142]

–: data not available, COD: chemical oxygen demand, VS: volatile solids.

Table 2
Effects of nanoparticles on the performance of biogas production processes.

Nanoparticle type	Inoculum	Feedstock	Period (d)	Methane production/rate	Effects of nanoparticles on the overall process performance	Refs.
Fe^0	Waste-activated sludge	–	17	70.6%	- Reduced the concentration of H_2S in biogas by 98.0% - Increased the content of methane in biogas by 5.1–13.2%	[158]
Fe^0	Anaerobic granular sludge	Basal medium	13.2	0.310 mmol CH_4 formed/mol Fe^0.d	- Increase in methane production. - Reduction in sulfate reduction. - Fe^0 enhanced the activity of methanogens.	[159]
Fe^0	*Dehalococcoides* sp.	Growth medium	20.8	275 ± 2 µmol	- Methane production increased relative to ZVIN-free controls. - Methanogens were biostimulated in the presence of ZVIN. - H_2 evolved from NZVI via cathodic corrosion was used as electron donor by methanogens.	[172]
Fe^0	Waste-activated sludge	–	36	217.16 mL/g VSS	- The use of 10 mg TSS ZVIN enhanced the methane production by 120%. - Low concentration of ZVIN promoted the population of microbes (bacteria and archaea).	[175]
Fe_2O_3	Waste-activated sludge	–	36	212.43 mL/g VSS	- The use of 100 mg/g TSS Fe_2O_3 enhanced the methane production by 117%. - Low concentration of Fe_2O_3 promoted the population of microbes (bacteria and archaea).	[175]
Fe^0	Digested sludge	Glucose	14	135 ± 2 mL	- ZVI inhibited methanogenic growth and methane production at 1 mM and above. - ZVI powder (30 mM) maximized the methane production.	[176]
Fe^0	*Dehalobacter* sp. *Sedimentibacter* sp. *Dehalogenimonas* sp.	Basal medium	30	–	- ZVIN below 0.05 g/L stimulated the dechlorination of mixed chloroethanes by ORB. - ORB are completely inhibited by ZVIN above 0.5 g/L.	[181]
Fe^0	Anaerobic granular sludge	Growth medium	6.25–8.3	9–10%	- Testing of Ag^0, Al_2O_3, CeO_2, Cu^0, CuO, Fe^0, Fe_2O_3, Mn_2O_3, SiO_2, TiO_2, and ZnO for inhibitory effects of methanogenesis. - Methanogenic activity was inhibited the most by Cu^0 and ZnO nanoparticles.	[182]
CuO	Anaerobic granular sludge	Growth medium	107	± 6 g COD CH_4 L^{-1} d^{-1}	- 20–30% of CuO NPs were used by methanogens during the anaerobic process. - Methanogenic species were inhibited by high CuO concentrations. - Methanogenic species were inhibited by high CuO concentrations.	[194]
γ-Al_2O_3	Anaerobic granular sludge	Inorganic salts	16.6	> 100 m-Eq/L	- Increased SMA in sludge incubations without γ-Al_2O_3, compared to the experiments which had 100 g/L of γ-Al_2O_3. - The SMA in incubations with γ-Al2O3 was not entirely inhibited, thus show that some bacteria were stimulated by the presence of γ-Al_2O_3 NPs.	[195]

-: no data, TSS: total suspended solids, ZVI: zero valent iron, ZVIN: zero-valent iron nanoparticles, ORB: organochlorine respiring bacteria, SMA: specific methanogenic activity.

calorific value of methane. In addition, they prevent the use of methane in natural gas grids [160–162]. Various approaches have been developed in order to remove these contaminants in biological processes [163,164]. ZVI nanoparticles are seen as promising adsorbents due to their remarkable properties such as high adsorption capacity, extremely small size, large surface-area-to-volume-ratio and high reactivity. This allows them to be used in the removal of many contaminants such as heavy metals, sulfides, polychlorinated biphenyls, aromatic hydrocarbons, chlorinated aliphatic and inorganic ions [165,166]. Furthermore, the ZVI nanoparticles exhibit a typical core-shell structure where the core consists of zero-valent iron (ZVI) or metallic iron nanoparticles, and the oxide-shell consists of iron oxides and hydroxides (FeOOH), as shown in Fig. 2. The core acts as an electron donor to compounds while the shell provides active sites for complex chemical reactions (chemisorption) and electrostatic interactions to occur [167–170]. However, iron oxides can possess properties of metals or ligands, depending on the pH of the medium. At low pH, the iron oxides becomes positively charged and reacts with negatively charged ligands (e.g. phosphate). At high pH (pH ~ 8), the iron oxides becomes negatively charged and can react with cations. Other notable characteristics of ZVI nanoparticles includes high solubility in water, excellent electron donating properties, and high structural stability, which makes them suitable for the removal of various contaminants (Hg^{2+}, Ni^{2+}, Zn^{2+}, H_2S, etc) as seen in Fig. 2 [167–171].

Xiu et al. [172] investigated the dechlorination effect of ZVI nanoparticles during the anaerobic process. It was demonstrated that the use of 1 g/L nanoparticles had a stimulatory effect on methane production. This resulted in high methane production of 58 ± 5 2 μmol to 275 ± 2 μmol. The nanoparticles were also instrumental in the inhibition of trichloroethylene dechlorinating bacteria, which competes with methanogenic archaea for molecular hydrogen [172]. The process of anaerobic digestion involves a syntrophic interaction between different microorganisms of archaeal and bacterial domains, which played an important role in the suppression of chlorine containing microorganisms [173,174].

Several studies were also conducted to investigate the effects of nanoparticles on microbial communities during anaerobic digestion processes. Wang et al. [175] evaluated the influence of four nanoparticle representatives (ZVI, Ag, Fe_2O_3 and MgO) on biogas production using waste activated sludge. The use of ZVI nanoparticles (10 mg/g TSS) and Fe_2O_3 nanoparticles (100 mg/g TSS) increased the biogas production by 120% and 117%, respectively, compared with the control. These results demonstrate that low concentrations of ZVI nanoparticles and Fe_2O_3 nanoparticles has a positive effect on the activity of methanogenic archaea. Yang et al. [176] observed that the addition of ZVI nanoparticles enhanced the population of methanogens in the anaerobic digester. Quantitative PCR results showed the dominance of *Methanosaeta* species (known to be the main producers of methane) in the presence of 30 mM ZVI nanoparticles. The authors also observed that ZVI powder (average size < 212 μm) increased the methane content due to the formation of hydrogen, which is used by hydrogenotrophic methanogens. Similar studies showed that the presence on nanoparticles favors the proliferation of methanogens because they promote direct interspecies electron transfer in syntrophic interactions of archaeal-bacterial species [177,178]. The addition of nanoparticles also favors the formation of intermediates (acetate, butyrate, formate, hydrogen, etc) which are essential in methane-generating pathways [179,180]. However, the methanogenic pathways are still dependent on the above mentioned properties of nanoparticles [179,180]. Koenig et al. [181]. observed that the combination of ZVI nanoparticles and organochlorine-respiring bacteria (ORB) could be used to detoxify chlorine containing compounds. A ZVI concentration below 0.05 g/L had a stimulatory effect on the growth of ORB, and this reduced the concentration of chlorine during the anaerobic process. On the other hand, Gonzalez-Estrella et al. [182] studied the impact of eleven nanoparticles (CeO_2, CuO, Mn_2O_3, Fe^0, TiO_2, Ag^0, Al_2O_3, Cu^0, ZnO, Fe_3O_4 and SiO_2) on methanogenic activity using anaerobic granular sludge. It was shown that Cu^0 and ZnO exhibited high inhibitory effects on methanogenic species. These nanoparticles achieved a 50% reduction in the activity of acetoclastic and hydrogenotrophic methanogens at 62 and 68 mg/L for Cu^0 nanoparticles; and 87 and 250 mg/L for ZnO nanoparticles, respectively. The influence of CuO and ZnO nanoparticles on biogas production was also investigated using cattle manure at mesophilic conditions (36 °C) [183]. Biogas production was inhibited by high concentrations of nanoparticles at 15–120 mg/L for CuO and 120–240 mg/L for ZnO, respectively. It was also observed that Fe_3O_4 and ZVI nanoparticles enhanced the digestion of slurry, which resulted in high biogas production [184]. Consequently, the addition of 20 mg/L ZVI nanoparticles and 20 mg/L Fe_3O_4 magnetic nanoparticles increased the biogas volume by 45% and 66%, respectively. Magnetic

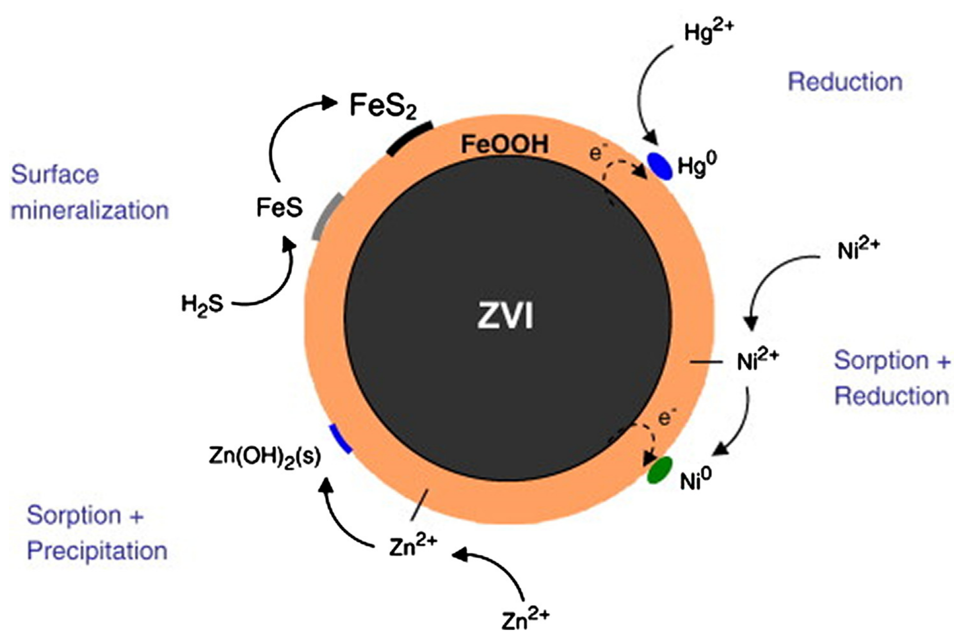

Fig. 2. The core-shell structure of ZVI nanoparticles and schematic illustrations showing the removal of various compounds such as Hg^{2+}, Zn^{2+}, Ni^{2+} and H_2S. Reprinted from Ref. [167], with permission from Elsevier.

nanoparticles also hold great potential in biofuels due to their significant properties such as large surface-area-to-volume-ratio, high solubility in water, high chemical stability, superparamagnetism and high recovery [185–188]. Researchers observed that the structure - and performance of these particles is highly dependent on the method of synthesis as well. Therefore, Stoeva et al. [189] proposed a novel method for the synthesis of composite magnetic nanoparticles using gold surface, silica core and magnetic inner layer (Fig. 3). In this approach, the positively charged amino-modified SiO_2 particles are conjugated with the negatively charged hydrophilic Fe_3O_4 nanoparticles (15 ± 1 nm) superparamagnetic, water-soluble Fe_3O_4 nanoparticles (step 1). This results in the formation of SiO_2-Fe_3O_4 nanoparticles (step 2). The Au nanoparticle seeds (1–3 nm) act as nucleation sites for the formation of the continuous Au-shell around the SiO_2-Fe_3O_4 nanoparticles, during the reduction of chloroauric acid ($HAuCl_4$), as shown in step 3 [189]. The authors also studied the morphology of these nanoparticles using transmission electron microscopy (TEM). Fig. 4A and B shows TEM images of amino-modified SiO_2 nanoparticles (200 nm) that are heavily loaded with silica-primed Fe_3O_4 nanoparticles (15 nm). The SiO_2-Fe_3O_4 nanoparticles were positively charged and formed electrostatic interactions with negatively charged Au nanoparticles (1–3 nm), which were formed during the reduction of $HAuCl_4$ with tetrakis(hydroxymethyl)phosphonium chloride (THPC) (Fig. 4C and D). Energy dispersive x-ray (EDX) characterization showed that these nanoparticles consisted of Fe, Si and Au precursors. Fig. 4E shows TEM images of the three-layer magnetic nanoparticles with smooth Au surfaces. It was also demonstrated that this synthetic approach can be functionalized with DNA molecules. Therefore, these properties make magnetic nanoparticles ideal adsorbents in biological processes [189].

The use of nanoparticles in anaerobic digestion processes also offers a symbiotic relationship because it allows microorganisms to acts as catalytic agents, whereby they can alter the oxidation state of the nanoparticle elements. This promotes the transfer of electrons and in turn allows various reactions to occur [190,191]. In addition, the nanoparticles provide a large surface-area-to-volume for microorganisms to bind in active sites of molecules and stimulates their physiological activities as highlighted earlier. This also favors the metabolism of various microbial communities, which promotes the formation of numerous mechanisms such as complexation, aggregation, etc [190–193].

2.3. Biodiesel production

Biodiesel presents many advantages due to its decreased CO_2 emissions, highly degradable nature and its production from various edible and non-edible oils [196,197]. Biodiesel production using non-edible oils (microalgal oils, plant oils and animal oils) has many socio-economic benefits because these feedstocks are considered as waste and are highly abundant [198,199]. Furthermore, they do not pose a threat to food security unlike edible-oils (sunflower oil, soybean oil, rapeseed oil, coconut oil, palm oil, groundnut oil, etc). This also makes the process of biodiesel to be commercially competitive due to reduced process costs [41,200].

The use of nanoparticles has emerged as a novel technology that can be used to achieve high yields in biodiesel production [201,202]. It has been shown that the incorporation of nanoparticles improves the catalytic efficiency during the transesterification process. Chen et al. [201] evaluated the effects of Fe_3O_4/ZnMg(Al)O magnetic nanoparticles in biodiesel production using microalgal oil. The catalyst exhibited excellent magnetic responsivity and a large surface-area-to-volume-ratio, which favored the production of biodiesel, and resulted in high yield of 94%. Furthermore, the biodiesel conversion was above 82% after seven cycles, and the nanocatalyst could be recovered. Similarly, Jeon et al. [203] used silica (SiO_2) and methyl-functionalized silica (SiO_2-CH_3) nanoparticles to maximize the growth of microalgal species (*Chlorella vulgaris*) for high lipid extraction. A maximum dry cell weight of 1.49 g/L was obtained using SiO_2-CH_3 nanoparticles. This value was three times higher than that of the control experiment. In addition, a maximum fatty acid methyl ester (FAME) of 1.00 g/L was extracted from the cells of *C. vulgaris* using SiO_2-CH_3 nanoparticles. It was also observed that the addition of 0.2% (wt) SiO_2-CH_3 nanoparticles enhanced the dry cell weight and FAME productivity by 210% and 610%, respectively. Tahvildari et al. [204] studied the effects of CaO and MgO nanocatalysts on biodiesel production from waste cooking oil. Experimental results showed that the use of both nanocatalysts maximized the biodiesel production yield. Consequently, a maximum biodiesel yield of 98.95% was achieved at a methanol-to-oil-ratio of 7:1, reaction time of 6 h, using 0.7 g of CaO and 0.5 g of MgO nanoparticles. Furthermore, Baskar et al. [205] studied the optimum process conditions for the transesterification of castor oil, with nickel doped ZnO nanocatalyst. A maximum biodiesel production yield of 95.2% was achieved at a methanol-to-oil-ratio of 8 mol/mol, catalyst concentration of 11.07% (w/w), temperature of 55 °C, and reaction time of 60 min, using the central composite design (CCD). Dantas et al. [206] evaluated the effects of Cu^{2+} doping in magnetic nanoferrites ($Ni_{0.5}Zn_{0.5}Fe_2O_4$) during the methyl transesterification of soybeans oil and achieved a biodiesel production yield of 85%.

Several studies also explored the effects of acid/base-functionalized nanoparticles on biodiesel production using different feedstocks. Wang et al. [207] successfully used acid-functionalized magnetic nanoparticles as a catalyst for biodiesel production. The acid-functionalized nanoparticles which consisted of sulfamic and sulfonic silica-coated crystalline Fe/Fe_3O_4 core/shell magnetic nanoparticles (MNPs) were synthesized and then used in the transesterification of glyceryl trioleate. These additives showed high catalytic activity, but sulfamic MNPs generated a higher catalytic activity with high biodiesel conversion of more than 95%. In another study, Hebbar et al. [208] used CCD to determine the optimum parameters for the transesterification of Bombax ceiba oil, using CaO as a nanocatalyst. A maximum biodiesel yield of 96.2% was achieved at a methanol-to-oil-ratio of 10.37:1 (mol:mol), catalyst loading of 1.5 wt%, reaction time of 70.52 min, temperature of 65 °C, and agitation speed of 600 rpm. A coefficient of determination (R^2) of 0.9936 was achieved with the CCD model, which indicated that the model was accurate in navigating the optimization space. In addition, it was shown that the nanocatalyst could be used up to five reaction cycles. Chiang et al. [209] used functionalized Fe_3O_4@silica core-shell nanoparticles for one-pot microalgae conversion to biodiesel. Three types of algae sources (dried algae, algae oil and algae concentrate) were evaluated for biodiesel production. The results showed that the functionalized Fe_3O_4@silica nanoparticles can achieve a high biodiesel yield of 97.1% using algal oil. Bet-Moushoul et al. [210] evaluated five types of Ca-based catalysts, supported with gold nanoparticles for biodiesel production. The studied nanocatalysts were CaO, egg shell, mussel shell, calcite, and dolomite. A maximum sunflower oil conversion of 97.5% was obtained at temperature of 65 °C,

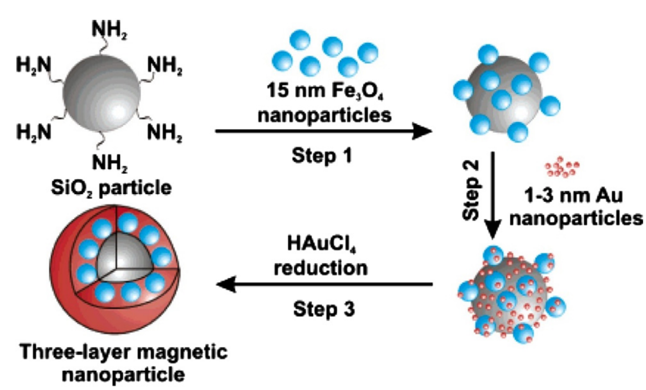

Fig. 3. Illustration of the preparation method of three-layer magnetic nanoparticles. Reprinted from Ref. [189], with permission from the American Chemical Society.

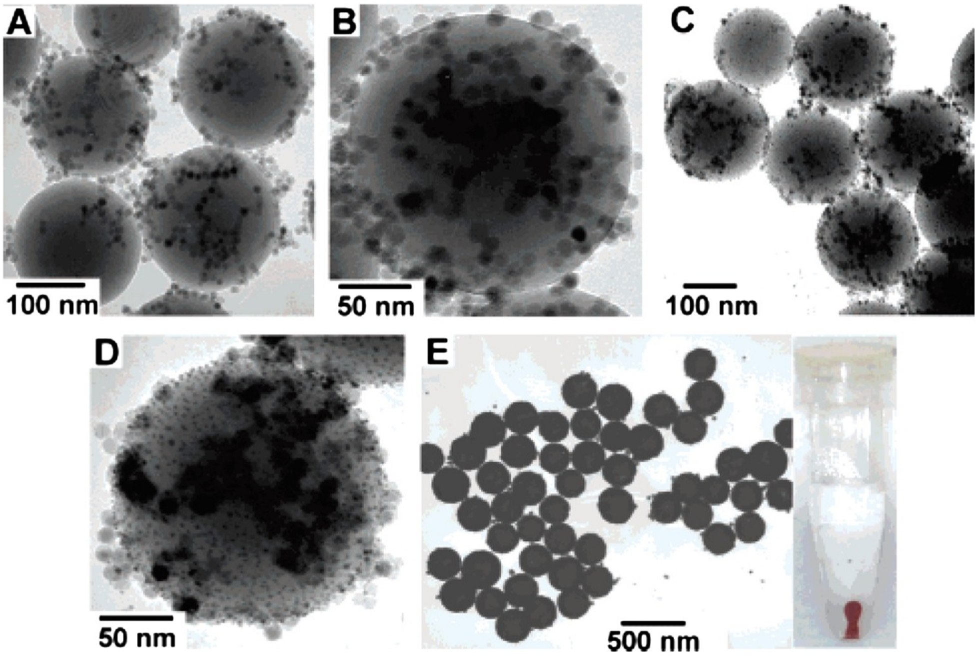

Fig. 4. TEM images of magnetic nanoparticles after the synthetic step. (A–B) SiO_2 nanoparticles conjugated with Fe_3O_4 nanoparticles to form SiO_2-Fe_3O_4. (C–D) SiO_2 particles covered with silica-primed Fe_3O_4 nanoparticles and coated with Au nanoparticles to form SiO_2-Fe_3O_4-Au seeds. (E) Three-layer magnetic nanoparticles produced in a single step process using nanoparticles from (C) and (D). Reprinted from Ref. [189], with permission from the American Chemical Society.

methanol-to-oil-ratio of 9:1, reaction time of 3 h, and catalyst loading of 3%, using calcite-Au nanoparticles. In addition, it was shown that the nanocatalyst could be used up to ten times without the loss of activity. The application of nanoparticles in biodiesel production ensures that the process is economically viable because the recovery and reusability of catalysts results in high biodiesel conversion efficiency as documented in these studies [209,210]. Table 3 summarizes the different nanocatalysts used in biodiesel production processes.

Besides the conventional biodiesel production methods, researchers are also exploring other techniques of producing biodiesel. One of the most attractive methods is the lipase-catalyzed transesterification process. This approach has gained a lot of attention due to its merits such as low energy demands, reusability of enzymes, and utilization of various feedstocks [211,212]. However, the high cost of lipase enzymes prevents their industrial application [213–215]. Immobilization methods are being used to stabilize these enzymes and also improve their recovery during transesterification [213,216]. The incorporation of nano-immobilized lipases is advantageous in biodiesel production because they provide a large surface-area-to-volume-ratio for enzymes to bind in active sites of molecules and functional groups during the process [217,218]. This results in high biodiesel conversion efficiency [219,220]. Moreover, nano-immobilized lipase biocatalysts exhibit Brownian motion, as compared to free enzymes, and exhibit higher activity [31,221,222]. Since this technology is still in its early stages, further investigations are necessary. This includes techno-economic assessments of nano-immobilized lipases as biocatalysts for large-scale biodiesel production processes. Studies that used these biocatalysts in biodiesel production are presented in Table 4.

Table 3
Nanocatalysts reported in biodiesel production processes.

Feedstock	Nanocatalyst	Reaction conditions	Yield (%)	Refs.
Castor oil	Ni doped ZnO	Temperature = 55 °C, time = 60 min, methanol/oil ratio = 1.8, catalyst loading = 11% (wt)	95.2	[205]
Soybean oil	$Ni_{0.5}Zn_{0.5}Fe_2O_4$ doped with Cu	Temperature = 180 °C, time = 1 h, methanol/oil ratio = 1:20, catalyst loading = 4% (wt)	85	[206]
Bombax ceiba oil	CaO	Temperature = 65 °C, time = 70.52 min, methanol/oil ratio = 30.37:1, catalyst loading = 1.5% (wt)	96.2	[208]
Sunflower oil	Calcite/Au	Temperature = 65 °C, time = 6 h, catalyst loading: 0.3% (wt), methanol/oil ratio = 9:1	97.58	[210]
Sunflower oil	$MgO/MgAl_2O_4$	Temperature = 110 °C, time = 3 h, methanol/oil ratio = 12, catalyst conc. = 3% (wt)	95.7	[223]
Tricaprylin	Carbon nanohorn dispersed with $Ca_2Fe_2O_5$	Temperature = 180 °C, time = 1 h, catalyst weight = 0,12 g, methanol = 3 g	100	[224]
Jatropha oil	Hydrotalcite particles with Mg/Al	Temperature = 44.85 °C, time = 1.5 h, anhydrous methanol = 40 mL, sulfuric acid = 4 mL, catalyst amount = 1% (wt), methanol/oil ratio = 0.4:1 (v/v)	95.2	[225]
Soybean oil	ZrO_2 loaded with $C_4H_4O_6HK$	Temperature = 60 °C, time = 2 h, methanol/oil ratio = 16:1, catalyst loading = 6% (wt)	98.03	[226]
Chinese tallow seed oil	KF/CaO	Temperature = 65 °C, time = 3 h, methanol/oil ratio = 12:1, catalyst loading = 3% (wt)	96.8	[227]
Palm oil	TiO_2-ZnO	Temperature = 50–80 °C, time = 5 h, palm oil = 21.86 g , methanol = 12.23 mL	98	[228]
Waste cooking oil	$SO4^{2-}/ZrO_2$	Temperature = 148.5 °C, time = 93 min, methanol/oil ratio = 12.7, catalyst loading = 2.9% (wt)	93.5	[229]
Rice bran oil	CaO	Temperature = 65 °C, time = 120 min, methanol/oil ratio = 30:1, catalyst loading = 0.4% (wt)	93.5	[230]
Rapeseed oil	$Na_2Si_2O_5$	Temperature = 65 °C, time = 120 min, methanol/oil ratio = 30:1, catalyst loading = 0.4% (wt)	97.8	[231]
Canola oil	KOH/calcium aluminate	Temperature = 65 °C, time = 4 h, methanol/oil ratio = 12, catalyst loading = 4% (wt)	91	[232]
Microalgae oil	CaO	Temperature = 70 °C, time = 3.6 h, methanol/oil ratio = 10:1, catalyst loading = 1.7% (wt)	86.41	[233]
Waste cooking oil	ZnO	Temperature = 60 °C, time = 15 min, methanol/oil ratio = 6:1, catalyst loading = 1.5% (wt)	96	[234]
Sunflower oil	$MgO-La_2O_3$	Temperature = 64.85 °C, time = 15 min, methanol/oil ratio = 18:1, catalyst loading = 60% (wt)	97.7	[235]

Table 4
Nano-immobilized biocatalysts reported in biodiesel production processes.

Feedstock	Microorganism	Nanocatalyst	Yield (%)	Refs.
Soybean oil	*Pseudomonas cepacia*	Fe_3O_4	88	[236]
Soybean oil	*Thermomyces lanuginosa*	Fe_3O_4	90	[237]
Sunflower oil	*Burkholderia*	Alkyl-celite	85	[238]
Rapeseed oil	*Pseudomonas cepacia*	Poly-acrylonitrile fibers	80	[239]
Soybean oil	*Pseudomonas cepacia*	Poly-acrylonitrile nanofibrous membrane	90	[240]
Canola oil	*Burkholderia cepacia*	$Fe_3O_4@SiO_2$	91	[241]
Waste vegetable oil	*Rhizomucor miehei*	Dendrimer-coated magnetic multi-walled Carbon nanotubes	94	[242]
Waste vegetable oil	*Candida antarctica*	$Fe_3O_4@SiO_2$	100	[243]
Waste vegetable oil	*Candida* sp.	Fe_3O_4 sub-microspheres	80	[244]
Palm oil	*Thermomyces lanuginosus*	Fe_3O_4	97.2	[245]
Olive oil	*Burkholderia* sp.	Fe_3O_4-SiO_2	> 90	[246]
Soybean oil	*Aspergillus niger*	$Fe_3O_4@SiO_2$	> 90	[247]
Olive oil	*Burkholderia* sp. *C20*	Alkyl grafted core–shell Fe_3O_4-SiO_2	95.74	[248]
Canola oil	*Candida Antarctica* *Thermomyces lanuginosus* *Rhizomucor miehei*	Epoxy-functionalized silica	98	[249]

2.4. Bioethanol production

Bioethanol is one of the most commonly used alternate fuels in the transport sector due to its economic and environmental benefits [250–252]. Its global production has increased in recent years i.e. it grew from 39 billion litres in 2006 to approximately 100 billion litres in 2017 [253]. Bioethanol has several beneficial properties such as (i) high octane number (~108), (ii) high evaporation enthalpy, and (iii) wide range of flammability for combustion purposes [254]. These characteristics allows bioethanol to be blended with hydrocarbon fuels derived from crude oil [254]. Currently, majority of the world's bioethanol is produced from edible crops such as corn, oats, wheat, barley, sugarcane, sorghum and rice [56,255]. During the fermentation process, these feedstocks are used alongside the inoculum (yeast or bacteria) to generate ethanol [56,255]. Therefore, ethanol that is produced from food crops is referred to as first generation bioethanol, and countries such as Brazil, China and USA are global leaders in bioethanol industry [56,255]. However, the use of edible crops poses a threat to food security [14,256]. This has reinvigorated researchers to look for alternative feedstocks [14]. Over the past decade, research has been focusing on processes that use non-edible feedstocks such as second generation bioethanol (rice straw, corn straw, grasses, sawdust, molasses, etc) and third generation bioethanol (algal biomass), in order to accelerate the development of bioethanol from non-edible materials. Amongst these feedstocks, lignocellulosic materials are seen as promising substrates for large-scale bioethanol production due to their abundance, renewable nature and affordability [52,56]. The annual global production of lignocellulosic biomass is estimated at 200 billion tons [52].

The production of bioethanol using biomass involves a complex process. It consist of four major steps which include biomass pretreatment, enzymatic hydrolysis, the fermentation process and ethanol production [56]. Nevertheless, the utilization of lignocellulosic feedstocks for bioethanol production is not yet commercially viable due to several constraints. Firstly, lignocellulosic biomass consist of a complex structure, i.e. cellulose (35–50%), hemicellulose (20–35%), lignin (15–20%), and other minor constituents [56]. The feedstock needs to be firstly broken down in order to access the cellulose and hemicellulose. Secondly, several inhibitors of *Saccharomyces cerevisiae* are formed during the pretreatment process. These include carboxylic acids, furans and phenolic compounds [257,258]. Moreover, plant-based materials consists of contaminants that disrupt the metabolism of *S. cerevisiae*, and lowers the bioethanol yield [259,260]. It has been shown in several studies that immobilization of enzymes can be used to overcome issues related to inhibitors in bioethanol production. Cherian et al. [261] immobilized cellulase in MnO_2 nanoparticles for improved conversion of sugarcane leaves to bioethanol. It was revealed that the immobilized cellulase was able to hydrolyze cellulosic materials over a wide range of temperatures (30–80 °C) and pH (4–8), and this resulted in high bioethanol yield (21.96 g/L). Furthermore, the enzyme had a binding efficiency of 75% and retained 60% of catalytic activity, even after five cycles. The MnO_2 nanoparticles provide a large surface-area-to-volume-ratio for enzymes to bind on active sites of molecules/functional groups as confirmed in similar studies [261]. Immobilization protects the enzymes against the inhibitory effects of intermediate metabolites such as organic acids and alcohols which are formed during solventogenesis [262,263]. It also allows enzymes to withstand the harsh environmental conditions in comparison to free enzymes. Beniwal et al. [264] immobilized β-galactosidase in silicon dioxide nanoparticles for the hydrolysis of whey and co-immobilized cultures of *Kluyveromyces marxianus* and *Saccharomyces cerevisiae* in a single-stage batch process. This experiment approach resulted in high bioethanol yield of 63.9 g/L. The immobilized β-galactosidase was reused up to 15 times during hydrolysis, without major loss in catalytic activity. Verma et al. [265] immobilized β-glucosidase in Fe_3O_4 nanoparticles for bioethanol production. The authors recorded a binding efficiency of 93% and more than 50% of catalytic activity after 16 cycles. Lee et al. [266] demonstrated that it is possible to immobilize β-glucosidase enzymes on polymer magnetic nanofibers for bioethanol production using cellulosic biomass. It was observed that the attachment of β-glucosidase on these polymeric materials stabilized the enzyme and allowed for its reusability.

Bioethanol production using microorganisms immobilized in nanoparticles is also documented in literature. For example, Ivanova et al. [267] immobilized cells of *S. cerevisiae* using magnetic nanoparticles. The immobilized cells showed a high bioethanol production rate with a productivity of 264 g/L.h during the fermentation process. Immobilization materials such as calcium and sodium alginate have also been evaluated for bioethanol production and were shown to be effective towards the enhancement of bioethanol yields [267,268]. Lee et al. [268] increased the production of bioethanol using cells of *S. cerevisiae* entrapped in calcium alginate. The immobilized cells produced an ethanol yield of 100%, while the free-suspended cells generated an ethanol yield of 88%. It is noteworthy to state that the processes did not contain inhibitory metabolites. Similarly, Galazzo and Bailey [269] observed that cells cultivated in an alginate matrix generated high ethanol production, which was 50% greater than that of free-suspended cells. In another study, Duarte et al. [270] studied the encapsulation of *S. cerevisiae* using both chitosan and calcium alginate as immobilization matrices. Maximum bioethanol concentrations of 32.9 ± 1.7 and 30.7 ± 1.4 g/L were obtained using calcium alginate and chitosan-covered calcium alginate beads, respectively. The cells were reused up to eight times and no contamination was observed due to the protection of the immobilization barrier.

Other immobilizing agents such as apple peels [271], corncob

[272], orange peels [273], sorghum [274] and sugarcane [275] are reported as well. The inorganic carriers include mineral clays [276], γ-alumina [277], natural polymers such as chitosan [278] or synthetic polymers such as polyvinyl alcohol [279], and polyacrylamide [280]. However, alginate matrices are favored because they use mild fermentation conditions, they are inexpensive, allow the reusability of cells, can resist contaminants and have a high porosity [281]. *Zymomonas mobilis* is another ethanologenic organism that have a huge potential in industrial bioethanol production due to its desirable characteristics such as high specific rate of sugar uptake, increased ethanol yield and non-requirements for aerobic conditions [282]. Researchers are also using novel metabolic strategies to make this bacterium a suitable candidate for large-scale production of bioethanol [283–285]. Some breakthroughs have already been achieved using this organism. For example, DuPont commercially produces ethanol using an engineered strain of *Z. mobilis* that can ferment xylose and other sugars [252]. Other methods of immobilization that are also used to improve the bioethanol yields are shown in Table 5.

3. Factors affecting the performance of nanoparticles in biofuel production processes

There are several factors that influence the performance of nanoparticles in biofuel production processes. These include the synthesis approach, synthesis temperature and pressure, pH of medium, etc [299]. Some of these process conditions are summarized below.

3.1. The synthesis approach

Several methods of synthesizing nanoparticles have been reported in literature. These include the co-precipitation method, thermal decomposition, microemulsion, hydrothermal synthesis, synthesis using biological organisms (fungi and algae), synthesis using plant materials, etc [300–302]. Each technique has its own benefits and limitations. Nevertheless, biological methods are highly recommended because they employ non-toxic and environmentally friendly materials, and have been demonstrated to have minimal inhibitory effects on biocatalysts during biofuel production processes. Furthermore, synthesizing nanoparticles from plants and bacteria is favored because this approach uses low energy and is less expensive [300–302].

3.2. Nanoparticle synthesis temperature

Temperature is an important parameter that is used in the synthesis of nanoparticles. The calcination temperature of metallic nanoparticles varies from 100 to 700 °C, depending on the method of synthesis [303]. Physical and chemical methods usually use high temperatures (> 300 °C), while biological methods employ moderate temperatures (< 100 °C), or even ambient temperature [304]. Temperature affects the overall morphology (pore size, shape and stability) of nanoparticles.

3.3. Nanoparticle synthesis pressure

Pressure is also a controlled variable during the synthesis of nanoparticles. Pressure is applied to the reaction medium to achieve a specific size, morphology and aggregation in nanoparticles [305]. High pressures have been shown to increase the size of nanoparticles [305].

3.4. Nanoparticles synthesis pH

It has been shown that the performance of metallic nanoparticles (Au, Ag, Cu, Pd, Zn, etc) is affected by the synthesis pH [306,307]. At pH values less than 7, aggregation of particles occur and improves the stability of nanoparticles. Therefore, the size and geometry of nanoparticles can be controlled by varying the pH during the synthesis of nanoparticles.

3.5. Size of nanoparticles

Various nanoparticles sizes, which ranges from 5 to 100 nm, have been reported in literature for biofuel production processes. The production yields depends on various factors, including the size of nanoparticles, and in each process, it is necessary to determine an optimal set of operating parameters. Important factors to consider are the size

Table 5
Immobilization carriers reported in bioethanol production.

Microbial strain	Substrate	Carrier	Ethanol production/rate	Refs.
Baker's yeast	Sugarcane leaves	MnO_2	21.96 g/L	[261]
Kluyveromyces marxianus	Cheese whey	Silicon dioxide	63.9 g/L	[264]
S. cerevisiae C12	Corn starch	Calcium alginate	264 g/L.h	[267]
S. cerevisiae KCTC 7906	Growth medium	Calcium alginate	100%	[268]
S. cerevisiae JAY 270	Growth medium	Calcium alginate	32.9 ± 1.7 g/L	[270]
S. cerevisiae JAY 270	Growth medium	Chitosan-covered calcium alginate	30.7 ± 1.4 g/L	[270]
S. cerevisiae AXAZ-1	Growth medium	Apples pieces	0.154 g/L	[271]
S. cerevisiae ATCC 24858	Growth medium	Corncob grits	6.95 g/L	[272]
Baker's yeast	Growth medium	Orange peels	150.6 g/L.d	[273]
Baker's yeast 3013	Growth medium	Sorghum bagasse	5.72 g/L.h	[274]
S. cerevisiae NCIM 3640	YPD medium	Sugarcane pieces	72.65–76.28 g/L	[276]
S. cerevisiae SCY008	Growth medium	Polyethyleneimine grafted	7.18 g/L.h	[286]
S. cerevisiae M30	Blackstrap molasses	Thin-shell silk cocoons	19.0 g/L.h	[287]
S. cerevisiae MTCC 174	Sugarcane bagasse	Sugarcane bagasse	0.44 gp/gs	[288]
S. cerevisiae MTCC 174	Sugarcane bagasse	Calcium alginate	0.38 gp/gs	[288]
S. cerevisiae MTCC 174	Sugarcane bagasse	Agar	0.33 gp/gs	[288]
S. cerevisiae CGMCC 2982	Food waste	Corn stalk	84.85 g/L	[289]
S. cerevisiae	YPD medium	Bacterial cellulose membrane	2.1 g/g.h	[290]
Baker's yeast	Growth medium	PEO/alginate/Ca	0.42 g/g	[291]
S. cerevisiae NCYC 1119	Blackstrap molasses	Polyurethane foam cubes	11 g/L.h	[292]
S. cerevisiae	Beet molasses	Calcium alginate	10.16 g/L.h	[293]
S. cerevisiae	Sweet potato	Sodium alginate	9·8 g/L	[294]
Z. mobilis	Growth medium	Calcium alginate and κ-carrageenan	50 g/L.h	[295]
Z. mobilis ATCC 10988	Starch	Sodium alginate	7.6 g/L.h	[296]
Z. mobilis CCM 2770	Growth medium	Poly-vinyl-alcohol	43·6 g/L.h	[297]
Z. mobilis CCT 4494	Basal medium	Calcium alginate	93.4 g/L	[298]

YPD: yeast extract-peptone-dextrose medium, PEO: poly-ethylene-oxide, Ca: calcium.

and concentration of nanoparticles introduced during the production process.

4. Conclusions and future recommendations

It is evident that nanoparticles could play a pivotal role towards the advancement of biofuel production processes owing to their beneficial properties as documented in this review. However, in order to accelerate their application in bioprocesses, many technical barriers needs to be addressed. These include (i) synthesizing nanoparticles that are non-toxic to microorganisms, (ii) using nanoparticles that are less expensive, and (iii) using nanoparticles that are environmentally friendly. Furthermore, the following recommendations are proposed for future studies:

- Screening of nanoparticles with a wide range of concentrations to understand their effects on microbial activity and to establish optimum process conditions.
- Application of nanoparticles with various shapes and sizes in order to understand their behaviour on the performance of bioprocesses.
- It is necessary to conduct pilot-scale studies in order to assess the viability of using nanoparticles for up-scaled biofuel production processes. This includes techno-economic assessments for feasibility purposes.
- There is also a need to conduct combined experimental and computational studies as to provide a fundamental understanding of some of the mechanisms involved in biofuel production reactions. There has been marked improvements in algorithms and computational power which can be harnessed for screening purposes and to identify suitable nanoparticles for biofuel production processes.

Appendix:. Definitions

Section 2.1:

(i) In the context of this review, substrate conversion is used to describe the breakdown of substrate/feedstock into molecular hydrogen and its constituents (VFAs and alcohols). This process is carried out by various biohydrogen-producing bacteria such as *Clostridium*, *Bacillus,* etc.
(ii) Biohydrogen yield is defined as the amount of hydrogen (volume or mol) produced per gram or per mol of substrate (glucose, COD, TVS, VSS, etc) consumed.
(iii) Biohydrogen production rate is defined as the amount of hydrogen (volume or mol) produced per gram of substrate consumed during a specific period of time (hour or day) within the bioreactor.

Section 2.2:

(i) Methane yield is defined as the amount of methane (volume or mol) produced per gram or per mol of substrate (glucose, COD, TVS, VSS, etc) consumed.
(ii) Methane production rate is defined as the amount of methane (volume or mol) produced per gram of substrate consumed during a specific period of time (hour or day) within the bioreactor.

Section 2.3:

(i) Biodiesel production is an alternative diesel fuel that is produced from animal and vegetables oils during the transesterification process at various process conditions.
(ii) Biodiesel conversion/yield is expressed as the concentration or fraction (%) of diesel during the transesterification process.
(iii) Catalytic efficiency is an important indicator used to measure the catalyst performance in terms of catalyst usability/recovery, biodiesel conversation efficiency, etc.
(iv) During the transesterification process, the triglyceride (animal fats or plant oils) is reacted with alcohol (methanol or ethanol) in the presence of a catalyst (acid or base) to form fatty acid alkyl esters (biodiesel) and glycerol.

Section 2.4:

(i) In this section, ethanol production is expressed as a ratio of grams per litre (g/L) or gram per gram (g/g). Whereas the ethanol production rate is the ratio of ethanol concentration (g/L) during a specific time (t or d).

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