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Review

Critical Review on Nanomaterials for Enhancing Bioconversion and Bioremediation of Agricultural Wastes and Wastewater

Bahare Salehi [1] and Lijun Wang [2,*]

[1] Joint School of Nanoscience and Nanoengineering, North Carolina Agricultural and Technical State University, 1601 East Market Street, Greensboro, NC 27411, USA; bsalehi@aggies.ncat.edu
[2] Department of Natural Resources and Environmental Design, North Carolina Agricultural and Technical State University, 1601 East Market Street, Greensboro, NC 27411, USA
* Correspondence: lwang@ncat.edu

Abstract: Anaerobic digestion (AD), microalgae cultivation, and microbial fuel cells (MFCs) are the major biological processes to convert organic solid wastes and wastewater in the agricultural industry into biofuels, biopower, various biochemical and fertilizer products, and meanwhile, recycle water. Various nanomaterials including nano zero valent irons (nZVIs), metal oxide nanoparticles (NPs), carbon-based and multicompound nanomaterials have been studied to improve the economics and environmental sustainability of those biological processes by increasing their conversion efficiency and the quality of products, and minimizing the negative impacts of hazardous materials in the wastes. This review article presented the structures, functionalities and applications of various nanomaterials that have been studied to improve the performance of AD, microalgae cultivation, and MFCs for recycling and valorizing agricultural solid wastes and wastewater. The review also discussed the methods that have been studied to improve the performance of those nanomaterials for their applications in those biological processes.

Keywords: agricultural wastes; circular economy; anaerobic digestion; microalgae; microbial fuel cells; nanomaterials

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1. Introduction

Agricultural production generates large amounts of animal manure, crop residues, and food processing wastes [1], and is responsible for 21% of greenhouse gas emissions [2]. Effective implementation of recycling and valorizing fertilizer nutrients, water, and materials in agricultural wastes can help the agricultural industry to develop a circular economy and transit to sustainable agricultural production [1]. Physical, chemical, and biological technologies have been studied to treat agricultural wastes. Among various waste treatment technologies, anaerobic digestion (AD), microalgae cultivation, and microbial fuel cells (MFCs) technologies are three widely studied approaches for simultaneous production of bioenergy products and treatment of wet agricultural wastes and wastewater [1].

AD is an effective technology with four main biological processes: hydrolysis, acidogenesis, acetogenesis, and methanogenesis for converting organic wastes such as manure and crop residues to biogas (a gaseous mixture of CH_4 and CO_2) as an alternative to natural gas, and digestate as organic fertilizers [3]. Cultivation of microalgae on agricultural wastewater has been considered as a promising technology for recycling energy, water, and fertilizer nutrients in wastewater [4–8]. MFCs can directly convert chemical energy stored in organic wastes into electricity via redox reactions under mild conditions. Agricultural wastewater is an ideal substrate for MFCs because of its high soluble organic content, high biodegradability, and abundant availability [9,10].

Microbes and microalgae are cell factories for the bioconversion of agricultural wastes. Various nanomaterials have been studied to improve the efficiencies of microbial and microalgae cell factories by providing micronutrients, promoting multiple phase mass transfer, preventing inhibition, immobilizing microbial cells, economically and efficiently harvesting cells, and promoting electron transfer in electrosynthesis. The objective of this article is to provide a critical review on the studies and applications of various nanomaterials for the enhancement of bioconversion and bioremediation of agricultural solid wastes and wastewater via AD, microalgae cultivation, and MFCs.

2. Recycling and Valorizing Agricultural Wastes and Wastewater

2.1. Agricultural Solid Wastes and Wastewater

Agricultural production generates large amounts of organic wastes and residues. In the United States, the amounts of manure produced by top three livestock of cattle, pigs, and chickens are 1166, 91, and 164 million tons each year, respectively. Traditional application of animal manure to soil as a fertilizer increases global climate change due to the emissions of methane, carbon dioxide, and nitrous oxide, and impairs ground and surface water due to the runoff of N and P in manure [11]. Agricultural production in the United States generated about 111 million dry tons of primary crop residues each year, 76% of which is corn stover, and the remaining 24% of which is wheat and other grain residues [1]. Many studies have shown that between 30% and 70% of the crop residues could be sustainably removed [12].

Water is a highly valuable natural resource. About 70% of global water withdrawn is used for producing and processing foods. On the other hand, about 80% of the 380 trillion liters of wastewater generated globally each year is discharged into water bodies without proper treatment [13]. Agricultural wastewater contains large amounts of nutrients and organic matters with high contents of total nitrogen (TN), total phosphorus (TP), and biological oxygen demand (BOD). For instance, typical swine wastewater contains 2000–30,000 mg/L BOD, 600–2100 mg/L TN including 400–14,000 mg/L NH_3-N, and 100–250 mg/L TP [14].

Agricultural wastes must be properly managed to avoid their associated environmental pollution, public health issues, and loss of valuable resources. Policymakers around the world have recently promoted the concept of the circular economy by preferentially avoiding, reducing, reusing, and valorizing wastes generated during economic activities to address the global problems of resource depletion and climate change. Innovative technologies for conversing and valorizing agricultural wastes are crucial in the circular economy and the transition to sustainable agriculture [15].

2.2. Bioconversion and Bioremediation of Agricultural Wastes

Agricultural wastes have high contents of organics, nutrients, and moisture, which are potential substrates for bioconversion and bioremediation using proper microorganisms. AD, microalgae cultivation, and MFCs have been considered as promising biological processes for transforming agricultural wastes into value-added products such as biofuels, bioplastics, and biopower.

Anaerobic digestion. AD is an effective technology for converting manure and other agricultural wastes to biogas and organic fertilizers. The biogas can be upgraded to renewable natural gas (RNG) by removing its CO_2 or burnt directly to produce heat and electricity [3,16]. The biogas productivity and digester stability are affected by the compositions and type of feedstocks, especially the carbon to nitrogen ratio and ammonia content, operating conditions such as temperature, solid content, and pH value, and digester configurations [3]. Therefore, it is necessary to enhance the performance of digesters to improve profitability and meanwhile, assure their environmental benefits. Co-digestion of various agricultural wastes, pretreatment of feedstocks, and micronutrient additives have been studied to enhance the biogas production [17]. AD can decompose organic solid wastes to produce biogas, but it generates a large amount of effluent with dissolved organic compounds (i.e., digestate). The direct use of the digestate as a fertilizer has even more negative environmental impacts, particularly global warming potential, acidification, and eutrophication than the use of chemical fertilizers [18]. Recovery of ammonia and phosphate in the digestate can avoid the runoff of ammonium and phosphate to water bodies from its direct land application [19]. Furthermore, biogas contains a large amount of CO_2, which needs to be removed to produce RNG [16].

Microalgae cultivation. Microalgae have been used for many environmental applications such as wastewater treatment and CO_2 sequestration, and commercial production of biofuels, biochar, bio-chemicals, bioplastics, feed, and fertilizers [4–8,20–22]. During microalgae photosynthesis, it is critical to supply CO_2 and remove O_2. High concentration of O_2 generated by algal photosynthesis reduces the algal growth due to photoinhibition and photorespiration [23]. The addition of CO_2 in algal culture can decrease pH value, supply carbon, and avoid phosphorus precipitation and ammonia volatilization during algal cultivation [24]. Open raceway ponds and closed photobioreactors are two main suspended microalgal cultivation systems. Low biomass density and difficulty in harvesting are major technical and economic obstacles for the commercialization of suspended microalgal cultivation. Attached microalgae growth systems by forming a thin layer of microalgal film onto a solid surface have been studied to reduce the harvesting cost of algal production [25]. Microalgae biofilm-based systems showed higher biomass productivity, higher harvesting efficiency, reduced water consumption, and lower energy requirement [26]. Extensive studies have revealed that the growth of microalgae in a biofilm-based system can be affected by many factors, including cultivating conditions, cell properties, and surface properties of the attachment materials such as hydrophobicity and microstructure [27,28].

Microbial fuel cells. MFCs can produce electricity from chemical energy stored in biodegradable organic wastes. In an MFC, electrochemically active microbes such as *Shewanella* sp. and *Geobacter* sp. are used to oxide organic matters at the MFC anode while oxygen is a typical electron acceptor at the MFC cathode [29]. The O_2 level at the MFC cathode significantly affects its performance [30]. Ion-exchange membranes are usually used for transporting protons from anode to cathode in an MFC [31]. MFCs are facing challenges in low power density and generation rate, and high capital costs. Therefore, economic electrodes, availability of the electron acceptor, and proton exchange membranes are needed to develop low-cost, large-scale MFCs [10]. Research found that MFCs emitted a high amount of ammonia when they are used for remediation of ammonium abundant wastewater such as swine and dairy wastewater [32]. Therefore, efforts also have to be made to reduce NH_3 emission from MFC anode.

2.3. Nanomaterials for Enhancing Bioconversion and Bioremediation of Agricultural Wastes

Microbes and microalgae are cell factories for the bioconversion of agricultural wastes into biofuels and biochemicals. Various nanomaterials have been studied to improve the efficiencies of microbial and microalgal cell factories. Zhao et al. provided a comprehensive review on using nanomaterials to increase the efficiency of chemical production by microbial cells. This review is focused on the applications of nanomaterials in AD, microalgae cultivation and harvesting, and MFCs for the bioremediation of agricultural wastes [33].

The use of nanomaterials in AD to facilitate direct interspecies electron transfer (DIET), prevent sulfur/ammonia inhibition, supply trace micronutrients, and immobilize active enzymes can be a useful strategy to improve the performance of an AD process [34]. Iron oxide nanoparticles could significantly increase the biogas production during AD by alternating microbial communities [35]. Nanostructured biochar and iron oxides were used to adsorb P from agricultural wastewater [36]. Magnetic nanoparticles have wide applications for harvesting microalgae and immobilizing microbial [37]. As carbon-based materials have good electron mobility, high surface area, high chemical stability, and relatively low prices, they have been used to make electrocatalysts and electrodes for MFCs [38]. Studies also showed iron oxide loaded onto biochar can form a nanocomposite for electrodes [39]. Microalgae can be used as a promising precursor to make bio-electrodes with a high N/C ratio that can enhance the bacterial attachment [40].

3. Nanoparticles for the Enhancement of Anaerobic Digestion

3.1. Nanomaterials for Facilitating Direct Interspecies Electron Transfer (DIET) in AD

Various nanomaterials with unique physicochemical properties including nano zero valent metals (nZVMs) (e.g., Fe, Ni, Cu, Co, Ag, Au), metal oxide NPs (e.g., ZnO, CuO, TiO_2, MgO, NiO, Fe_2O_3), carbon-based nanomaterials (e.g., graphene, diamond, nanotube, and nanofibers), and multi-compound NPs have been studied as additives to improve the AD performance [34,41]. However, nanomaterials can have positive and negative effects on the performance of AD through interactions with feedstock and microorganisms, depending on their compositions and concentrations [34]. Table 1 summarized the effects of some nanoparticles on AD performance.

Table 1. Effects of various nanoparticles (NPs) in the forms of nano zero valent iron (nZVI), metal oxides, carbonaceous, and multi-compound on AD performance.

Substrate	Nanoparticles	Concentration/ Average Size	Effects on AD	Refs.
Sewage sludge	nZVI	0.1% sludge/160 nm	• Increasing in methane yield by 25.2% • Removal efficiency of COD by 54.4%	[42]
	Commercial iron powder	1.6% sludge/0.2 mm	• Increasing in methane yield by 40.8% • Removal efficiency of COD by 66.2%	
Raw manure	nZVI	20 mg/L/9 nm	• Enhancing the biogas and methane volume by 1.45 and 1.59 times, respectively, compared to those of the control.	[43]
	Fe_3O_4	20 mg/L/7nm	• Enhancing the biogas and methane volume by 1.6 and 1.96 times, respectively, compared to those of the control.	
Digested sludge	nZVI	30 mM/55 nm	• Decreasing the methane production by 69% due to the increasing soluble COD, volatile fatty acids, and accumulation of hydrogen.	[44]
Raw manure	Co NPs	1 mg/L	• Increasing the biogas and methane yield by 1.7 and 2 times respectively, compared to the control sample.	[45]
	Ni NPs	2 mg/L	• Increasing the biogas and methane yield by 1.8 and 2.17 times respectively, compared to the control sample.	
	Fe NPs	20 mg/L	• Increasing the biogas and methane yield by 1.5 and 1.67 times respectively, compared to the control sample.	
	Fe_3O_4 NPs	20 mg/L	• Increasing the biogas and methane yield by 1 and 2.16 times respectively, compared to the control sample.	
Waste-activated sludge	nZVI	10 mg/g TSS/<50 mm	• Increasing methane production to 120%, compared to the control.	[46]
	Ag NPs	100 mg/g TSS/<100 nm	• Increased methane production to 117%, compared to the control.	
	Fe_2O_3 NPs	500 mg/g TSS/< 30nm	• Increasing methane production to 73.52%, compared to the control.	
	MgO NPs	500 mg/g TSS/<50 nm	• Increasing methane production to 1.08%, compared to the control.	

Table 1. *Cont.*

Substrate	Nanoparticles	Concentration/ Average Size	Effects on AD	Refs.
Waste-activated sludge	nZVI	0.6–1 g/L	• Enhancing the hydrolysis and acidification by destroying the microbial cell integrity. • Increasing biomethane production. • Increasing VFAs and acetic acid production.	[47]
		4 g/L	• Enhancing the hydrolysis and acidification by destroying the microbial cell integrity. • Maximum VFAs and acetic acid production. • Inhibiting methanogens' activity by long-term accumulation of H2.	
		10 g/L	• Decreasing VFAs and acetic acid production. • Inhibiting methanogens' activity by long-term accumulation of H2.	

Iron-based nanoparticles have been extensively studied to enhance the AD performance. nZVI and Fe_3O_4 NPs have been used as additives to enhance the conversion efficiency and methane generation of AD. However, their effects on the performance of microorganisms are different owing to their physical and chemical properties. The addition of nZVI has showed an increase in the methane and hydrogen production in AD of municipal wastewater and industrial wastewater from brewery and sewage plants [47]. It was reported that the addition of Fe_3O_4 NPs at a 7 nm size and 100 ppm concentration increased methane production by 234% due to the presence of non-toxic Fe^{3+} and Fe^{2+} ions [41]. The main effect of iron NPs in an AD system is to change the interspecies electron transfer in the syntrophic process of AD in which butyrate or hydrogen are used to produce methane. The nZVI can serve as a suitable low release electron donor for methanogenesis in an AD process, resulting in the increase of biogas yield. The magnetite Fe_3O_4 NPs in an AD system can act as the electron conduit when the particles are attached to the membrane surface of different cells to accelerate electron transfer among different microorganisms, leading to the improvement of methane generation [48]. Another positive effect is the Fe^{2+}/Fe^{3+} which can promote the growth of microorganisms. Other properties including magnetism, absorptivity, and biocompatibility of Fe_3O_4 NPs which can strengthen the digestion efficiency of pollutants in AD. Fe_3O_4 NPs have been applied in the AD treatment of industrial, municipal, and agricultural wastewater, as well as the solid waste produced from agricultural and municipal activities. Aulenta et al. discovered that the kinetics during the AD of trichloroethene (TCE) dichlorination was increased by the addition of a small amount of Fe_3O_4 NPs at 10 mg Fe/L because of the promoted electron transfer in the dechlorinating culture and the enrichment of *Desulforomonas* species in microcosms [49]. The positive effects of Fe_3O_4 NPs on AD were also demonstrated by the increase in the H_2 production and biogas yield [50]. Similar to nZVI, Fe_3O_4 NPs could also remove heavy metal pollutants such as Cr(VI) in the wastewater due to their adsorptive capacity [51,52]. However, the effects of nZVI and Fe_3O_4 NPs on methane production depend on their concentration. The inhibitory impact of nZVI and Fe_3O_4 NPs at high concentrations on methanogenesis can be attributed to the deactivation of bacteria and the damage of bacterial cell membrane [51].

Studies have shown that ZnO, CuO, Mn_2O_3, and Al_2O_3 significantly reduce biogas production rate that may be attributed to the toxicity of these materials. For example, the use of 15 mg/L CuO NPs decreased the biogas production by 30%. However, some metal oxide NPs such as TiO_2 and CeO_2 at proper concentrations can enhance the biogas production. For example, it was reported that the biogas production increased by 10% by using TiO_2 NPs at a 7.5 nm size and 1120 mg/L concentration. However, the effects of metal oxide NPs on the biogas production depend on their concentrations in the reactor and digestion time. These metal oxide NPs have shown greater inhibitory effect on acetoclastic methanogenesis than hydrogentrophic methanogenesis. The toxicity of metal oxide NPs increases with time due to the increase of the released metal ions [51]. The addition of silver or gold nanoparticles results in either a decrease or no change in biogas production rate, depending on their concentrations in the reactor [51].

The addition of micro/nano fly and bottom ash from the thermochemical conversion of biomass and coal showed a considerable increase in biogas production, but the addition of fullerene (C60) and silica (SiO_2) nanoparticles, and single-walled carbon nanotubes had no effect on biogas production. The ZnFe nanocomposite can significantly improve methane production by up to 185%. Moreover, ZnFe with 10% carbon nanotubes (ZFCNTs), and ZnFe with 10% C76 fullerene (ZFC76) showed a positive effect on retention time and enhanced methane production up to 162% and 146%, respectively [41].

Nanostructured carbonaceous materials such as biochar have also been studied to strengthen the AD performance and improve the treatment efficiency of organic wastes. However, the types of biochar tested so far are very limited and the exact mechanism remains unclear. Zhang et al. investigated the effects of potassium phosphate- and magnesium-modified biochar and the biochar particle size on AD of cattail. They found that that the addition of potassium phosphate-modified biochar with a particle size smaller than 1 mm was the most conducive to methane production, increasing the biogas production by 18.3–20.1%. The use of biochar doped with 2 M $MgCl_2$ and calcined at 800 °C resulted in a 21.1% increase of specific methane productivity compared with AD without biochar. However, the direct use of raw biochar produced by the pyrolysis of pine wood in AD showed an adverse effect on the methane production. The increased buffer capacity, nutrients released by the biochar, enhanced electron transfer and better aggregation function of small particles may contribute to the improved methane production [53].

3.2. Nanomaterials for Preventing Sulfur/Ammonia Inhibition in AD

The required elements for microorganisms can be categorized as macro-elements (such as carbon, hydrogen, oxygen, nitrogen, and sulfur) and micro-elements (such as cobalt, zinc, and copper). Regarding the macronutrients, it is crucial to control their optimum contents in the culture medium to prevent the overloading or starving condition. Although these elements are needed for microbial growth, their high concentrations can change their stimulatory effect to inhibitory impact on bacterial growth [54]. Furthermore, the formation of H_2S from sulfur, and ammonia or ammonium from nitrogen during AD inhibits microbial growth [55]. The removal of those inhibitors can not only improve the quality and quantity of the produced biogas, but also protect the equipment from the corrosion [55]. Various nanomaterials have been studied to control the inhibitory effect of H_2S during AD [45,55–57]. It was reported that the addition of $FeCl_2$ could control the formation and inhibitory effect of H_2S [45]. Zinc oxide (ZnO) NPs can effectively decrease the H_2S generation during AD due to the formation of zinc sulfide (ZnS) [57]. Although silver is toxic to a large number of microorganisms, the high concentration of silver nanoparticles (40–43 mg/L) does not have any inhibitory effect on methanogens due to oxysulfidation and sulfidation of silver NPs in an anaerobic medium which leads to the precipitation of silver NPs in the nontoxic form of AgS [56].

Moreover, it was demonstrated adding one gram of nZVI can remove 12.56, 14.77, 391.02, and 488.95 mg H_2S at a room temperature of 100 °C, 200 °C and 250 °C, respectively. The addition of nZVI to AD can enhance the quality of the produced biogas by decreasing its H_2S due to the formation of non-volatile sulfur containing complexes [55]. nZVI can also enhance biomethane production by minimizing the toxic and harmful effect of H_2S in AD by reacting with sulfur to make FeS compound: $Fe^0 + H_2S \rightarrow FeS + H_2$ [42]. Furthermore, it was shown Fe^{2+} plays a key role in the assembly of the iron-sulfur clusters and electron transfer in cellular redox activity [46]. Suppressing the H_2S formation, gradually releasing Fe^{2+} and Fe^{3+} for electron transfer, and increasing pH stability by the nZVI improve the AD performance [34]. Generally, the inhibitory action of iron against H_2S can be categorized as:

(1) Forming FeS via the reaction between zero valent iron and H_2S, (2) Forming FeS and FeS_2 via the reaction between FeOOH and H_2S, and (3) Precipitating of dissolved sulfide via the reaction between HS^- and Fe^{3+} (reactions (1)–(3)) [58].

$$Fe^0 + H_2S \rightarrow FeS + H_2(g) \quad (1)$$

$$2FeOOH + 3H_2S \rightarrow FeS + FeS_2 + 4H_2O \quad (2)$$

$$HS^- + 2Fe^{3+} \rightarrow S^0 + 2Fe^{2+} + H^+ \quad (3)$$

Adding nanomaterials, especially metallic micro-elements such as nZVI can not only reduce the H_2S content in produced biogas, but also change the microbial structure [57]. The addition of iron NPs in AD can produce iron sulfide and iron disulfide to immobilize free sulfates, which subsequently decreases the population of sulfate-reducing bacteria (SRB), the main competitors of acetogenic and methanogenic bacteria in AD. Since SRBs are considered as the only biological source of H_2S production inside the AD, decreasing the SRB microbial population can control the H_2S production and increase the biogas yield in AD [57].

3.3. Nanoparticles as Trace Micronutrients

Trace metals can be considered as micronutrients to improve the AD performance and stability. As the concentrations of these elements including iron, nickel, cobalt, zinc, and copper in a culture medium are usually lower than their optimum levels, there is a need to provide their additives to the culture medium [45]. Nano-additives can improve the AD process by providing active sites for microorganisms and serving as an adsorbent for adsorbing inhibitors. Nano-additives with metallic trace elements (such as iron, nickel, and cobalt) at their optimum concentrations can positively influence the AD process and biogas production by providing key nutrients and essential constituents of enzymes and co-enzymes [57]. As the trace metals can stimulate and stabilize an AD process through their roles as crucial constituents of enzyme and cofactor, they are needed for most of the reactions in an AD process [45]. It was demonstrated that methanogenic bacteria need iron, cobalt, zinc, and nickel during enzyme synthesis. Research showed that nZVI could improve the AD performance not only by acting as an electron carrier, but also by promoting the growth of methanogens and consequently, higher chemical oxygen demand removal [45]. Furthermore, the additive of iron-based NPs can increase the concentration of energy-favorable volatile-free acids (VFAs) including acetate and butyrate, and release protons through their metabolic pathways, leading to the improvement of the methane production. Therefore, trace metals in a culture medium can not only decrease the lag phase, but also minimize the required time to achieve the highest biogas and biomethane generation during AD [45].

Many of conductive NPs affect the AD process by being part of requisite enzymes [55]. The released metal oxide ions are preconditioned for enzyme and cofactors in the AD biological processes. For instance, cobalt and nickel are coenzymes for methanogenic bacteria and methanogenic archaea, respectively [55]. In fact, cobalt acts as metallic activators for methanogenic enzymes [34]. Cobalt is considered as a structural ion in enzymatic transesterification [55]. Furthermore, cobalt is an essential coenzyme of B12 [45]. Nickel is a crucial cofactor for Ni-Fe hydrogenases, carbon monoxide dehydrogenase, methyl CoM reductase, and urease [45]. Nano nickel, especially in the form of nickel oxide, can enhance the biogas production by providing Ni^{2+} for hydrogenase and acetyl-CoA synthetase (ACS) that catalyze the conversion of acetyl-CoA to acetaldehyde [57].

Moreover, zinc and copper are coenzyme for enzymatic transesterification and biological electron transfer, respectively [55]. Zinc-based nanomaterials by involving the zinc-related enzymes such as ADH in converting acetaldehyde to ethanol, can also improve the biogas production. The addition of zinc-based nanomaterials can simulate the conversion of acetaldehyde into acetic acid and protons by inhibiting the activity of *Thermoanaerobacterales* bacteria in converting acetaldehyde to ethanol [57]. Iron, in the forms of nano-Fe, nZVI, nano Fe_2O_3, and nano Fe_3O_4, are considered as the most important additives for improving the AD performance due to their high conductivity and reactivity, low toxicity, and low cost [57]. nZVI, as an electron donor, could improve the enzymatic activity in acetic acid fermentation and propionic acid degradation [47].

The effects of the additives of trace metals on the AD performance strongly depend on their dosages and size, pH, and type of feedstocks. The high dosage of the trace elements can be toxic to the microorganisms and thus inhibit the AD process [45]. Research also showed that micronutrients at a nanoscale were more effective than those at a microscale attributing to the higher surface to volume ratio, higher reactivity, and higher self-assembly capability of nanoparticles [57]. For instance, it was shown that iron oxide NPs enhanced the biogas production better than non-nanoscale iron particles through shifting the main fermentation pathway from butyrate to acetate/butyrate with higher glucose utilization efficiency [57]. Research showed that the decrease in pH during a fermentation or acidification process increased the number of released ferric ions (Fe^{2+}) from ironic nano-compounds and subsequently improved the bioavailability of iron compounds for microorganisms. Although there was the linear correlation between iron-based NP dosage and biogas production when the iron was below the upper limit concentration, concentrations above the tolerant limit led to bacterial cell lysis and process inhibition [57].

3.4. Nanomaterials for Immobilizing of Enzymes and Microorganisms

Immobilization is described as a process to attach or entrap various types of biocatalysts including enzymes and cells with plant, animal or microbial origin on solid support or matrix [59]. It is a popular technique to improve the performance of enzymes and microorganisms by attaching or entrapping them on a carrier physically or chemically [59]. Enzymes are highly active biomolecules that have high potentials for wide applications in various scientific and industrial fields to enhance the speed of catalytic reactions owing to their high efficiency, biodegradability, biocompatibility, and high substrate specificity and selectivity. The industrial applications of free enzymes are limited due to their low operational or chemical stability, low storage stability, difficulty in their recovery and reusability, and high production cost. Immobilization of enzymes on solid supports can not only enhance their thermal and pH stability, but also facilitate their recovery and reuse [60].

After the first industrial enzyme immobilization which was developed in 1960s for aminoacylase, several techniques and modifications have been studied to enhance the performance, efficiency, reusability, and stability of immobilized enzymes, and decrease the production cost. The solid support and immobilization methods have gained considerable attentions. The solid support or matrix should have high biocompatibility, reusability, and surface area, and favorite surface chemistry for suitable and stable enzyme loading. Nanomaterials with specific functional groups and trace elements can significantly enhance the self-assembly of the enzyme-matrix hybrid which leads to higher efficiency and stability [60]. Microbial immobilization is a technique for restraining microbial biomasses in the specific form by attaching or entrapping them on solid matrix/support to promote their applications. Microbial immobilization is advantageous over free microorganisms in many scientific and industrial applications, especially by adsorbing heavy metals on the solid support, facilitating catalyst recovery, regeneration, and recycling, and improving stability and selectivity. Nanomaterials with a high surface area and specific physicochemical properties offer the great possibility to be used as flexible and versatile supports for immobilizing microorganisms. Research showed that attaching microorganisms on magnetic nanoparticles for the removal of toxic pollutants in wastewater not only increased the sorption capacity to adsorb pollutants in the wastewater, but also facilitated the separation of the cells from the wastewater using a magnetic field [59]. It was reported that the immobilization of microorganisms on conductive nanomaterials such as nZVI and nano carbonaceous materials could improve the methane production by eliminating the required enzymatic pathways for producing hydrogen or formate as an electron carrier, and replacing mediated interspecies electron transfer (MIET) with direct interspecies electron transfer (DIET) [34,61].

Enzymatic and microbial immobilization onto NPs may have positive or negative effects on their activity depending on the NP concentrations and immobilizing technique. The activity of microorganisms and enzymes can be improved by controlling the concentration of NPs. NPs at too high concentrations cannot improve the AD performance, but inhibit the microbial growth and enzyme activity by disrupting the cell integrity and enzyme assembly [34]. Generally, the inhibitory effect of NPs can be attributed to the cell membrane defection, enzyme inactivation, and protein dephosphorylation. Additionally, immobilization technique plays a key role in enzyme and microbial activities. The improper immobilization of enzymes would negatively affect their 3D structure, which leads to the decrease of their chance to interact with substrates and the subsequent decrease of their catalytic efficiency. On the other hand, proper immobilization of microorganisms can decrease the agglomeration of microorganism and thus enhance their growth and activity [34].

4. Nanoparticles for the Enhancement of Microalgae Cultivation

The first generations of biofuels derived from edible oil seeds, food crops, and animal fats, and the second generation of biofuels derived from low-value feedstocks such as non-edible oilseeds, used cooking oil, and lignocellulosic biomass have several disadvantages as alternative fuels including the destruction of vital soil resources, deforestation, and the use of large amounts of fresh water and arable land for the supply of those feedstocks. The third and fourth generations of biofuels by taking the advantage of algae and algae/microbes, respectively, offer several advantages over the previous generations of biofuels including high productivity and growth rate, short harvesting cycle (i.e., one to ten days), higher carbon sequestration capacity (10 to 50 times higher than terrestrial plants), less water and land requirements, high oil yield per acre, having the capacity to grow in the waste stream and extreme weather conditions, and no competition with food chain [62–64]. In spite of the mentioned advantages, more studies are needed to improve the microalgae cultivation for the large-scale economic production of biofuels by increasing their productivity, lipid content, and usage efficiencies of CO_2 and light [63]. Among various methods, there is an increasing attention to add functional nanomaterials to algal culture to improve CO_2 adsorption and light conversion efficiency for enhancing photosynthesis and algae growth. On the other hand, some destructive impacts of nanomaterials on algae growth were reported which depended on their concentrations and characteristic properties (e.g., size, crystal structure, and oxidation state), culture medium, and algae species. The effects of nanoparticles at low and high concentrations on microalgae were summarized in the literature as shown in Figure 1 [63].

4.1. Metallic Nanoparticles as Micronutrients for Algal Cultivation

Trace metals play a key role as micronutrients in microalgae growth. Their effectiveness depends on their concentrations in the culture media and their synergy or antagonistic effect with other environmental factors [62]. However, the enhancement of algal growth and lipid production strongly depends on the type and concentration of nanomaterials. Among various nanomaterials, iron has received considerable attentions due to its low toxicity, biocompatibility and high effectiveness. Microalgae require iron as an essential micronutrient in their fundamental cellular functions of photosynthesis and respiration [65]. As shown by Pádrová et al., adding a trace amount of nZVI (1.7 to 5.1 mg L^{-1}) could increase the growth of green algae (*Desmodesmus subspicatus*, *Dunaliella salina*, *Parachlorella kessleri*, and *Raphidocelis subcapitata*) and eustigmatophycean algae (*Nannochloropsis limnetica* and *Trachydiscus minutus*) [62]. Iron is a vital regulatory element in the gene expression and metabolism of algae. The presence of iron in the culture media can prolong the exponential growth phase and enhance the final cell density [62]. Iron plays a critical role in fundamental cellular functions by acting as a cofactor of key enzymes in photosynthesis and respiration. It can promote chlorophyll biosynthesis and biomass growth by activating the *Crd1* enzyme which plays a key role in the Calvin Benson cycle [63].

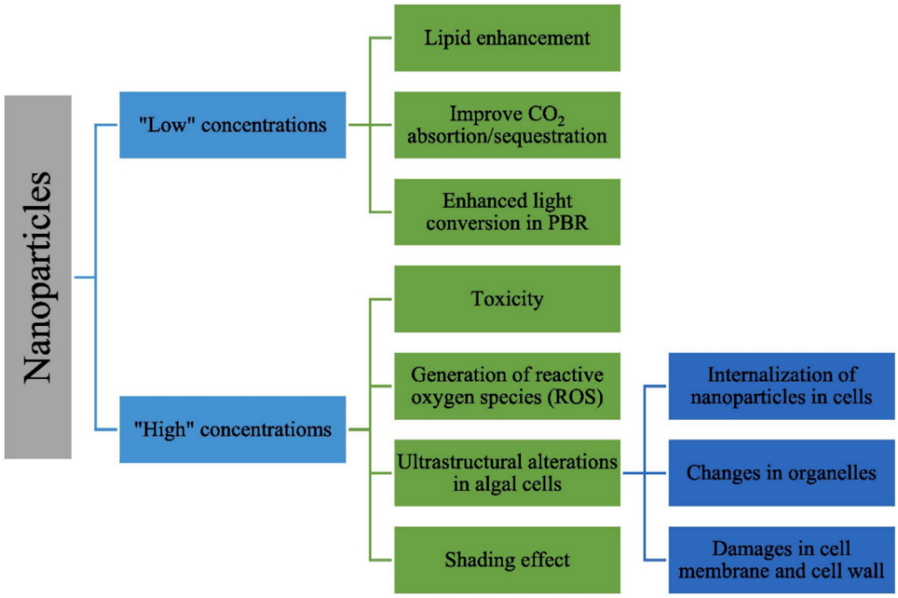

Figure 1. Effects of nanoparticles on microalgae (reprinted with permission of Elsevier) [63].

The increase of the iron content of algal culture leads to the simultaneous enhancement of the growth rate and lipid content in some microalgae species [62]. Pádrová et al. found that the addition of 1.7–5.1 mg L^{-1} of nZVI in the culture media for green algae *subcapitata* and *eustigmatophycean* algae enhanced the growth of those algae, and 5.1 mg L^{-1} nZVI could dramatically increase lipid accumulation [66]. Kadar et al. showed the lipid enhancement in *Tetraselims suecica* and *Pavlova lutheri* by the rate of 41.9% and 46.34%, respectively, after exposing to uncoated nZVI and coated nZVI powder [67]. Pádrová et al. in another study reported the addition of 5.1 mg/L nZVI to the *Trachydiscus minutus* and *Desmodesmus subspicatus* cultures increased the lipid content by about 9% and 38%, respectively. They claimed that nZVI could provide a suitable source of iron to enhance the cell growth and lipid contents and induce changes in lipids' metabolic pathways resulting in the alteration of the lipid composition [66]. Therefore, iron, especially nZVI, may be a suitable source for the increase of microalgae growth and algal lipid production, and alternation of algal lipid profile by increasing polyunsaturated fatty acids contents [66]. Another study further showed that the growth of the algae was even favored by the iron nanoparticles in comparison with their bulk analogues [67].

Although increasing iron concentration below a given threshold can increase the growth rate and lipid content, iron at concentrations above the threshold negatively impacts the algal biomass and lipid production [62]. Abd El Baky et al. found the concentration of $FeCl_3$ below 20 mg/L increased the total lipid accumulation, total lipid productivity, and biomass production of *Scenedesmus obliquus* by 28.13%, 95.35 mg per day, and 1.25 mg per liter, respectively, in the period of 18 days [68]. Cao et al. found that the optimum concentration of $FeCl_3 \cdot 6H_2O$ for the highest lipid content and growth rate of *Chlorella minutissima* was between 0.05 to 0.1 mM [69]. Most of the studies suggest that the increase of iron concentrations can increase the algal growth rate and lipid content but the concentrations above 0.002 g L^{-1} and 0.001 g L^{-1} have negative impacts on biomass and lipid production, respectively, due to inhibitory effects [62]. Owing to the high activity, iron NPs can produce various reactive oxygen species (ROS) via Fenton-type reactions that cause oxidative injury to cells via lipid peroxidation and oxidation of thiol groups of proteins and DNA [70].

Algal growth and lipid production are also affected by the environmental stress. The typical response of algae to environmental stress, especially nutrient shortage, is to accumulate a tremendous amount of carbon in the forms of carbohydrates and lipids for self-protection against damage. In the case of lipid accumulation under an environmental stress, the contents of most saturated and monounsaturated fatty acids increase and the content of polyunsaturated fatty acids associated with polar membrane decreases, which leads to the decrease in cellular growth [63]. Several studies showed the additives of nanomaterials could improve algal lipid production via induced stress [66,68,71]. The addition of SiC NPs under xenon illumination can improve lipid biosynthesis through inducing oxidative stress and enhancing the activity of acetyl-CoA carboxylase which is a key enzyme for catalyzing the lipid biosynthesis. Although the SiC NPs at an optimal concentration of 150 mg/L could increase lipid content by 40.26%, the TiO_2 and TiC NPs showed the inhibitory effect on the same algae [71].

4.2. Nanoparticles for CO_2 Supply

Microalgae can fix and convert atmospheric CO_2 to oxygen and biomass through photosynthesis. By considering the role of CO_2 as a carbon source in green algae cultivation, the improvement of CO_2 biofixation can increase the algal productivity and atmospheric CO_2 mitigation [72].

pH is an important factor that affects the CO_2 fixation. Alkaline pH can activate rubisco enzyme which is responsible for CO_2 fixation through the Calvin cycle. Therefore, alkaline pH can enhance algal biomass yield and subsequent photosynthesis efficiency. In fact, photosynthesis and microalgae growth lead to alkalize the culture medium. The generated OH^- ions in reaction with CO_2 can form bicarbonate ($CO_2 + OH^- \leftrightarrow HCO_3^-$) which can further be used as carbon sources for microalgae growth. However, an excessive amount of CO_2 entering the culture would acidify the culture medium through the formation of carbonic acid ($CO_2 + H_2O \leftrightarrow H_2CO_3$). Acidic pH decreases the activity of rubisco enzymes which will decrease the CO_2 biofixation efficiency and result in CO_2 loss. Nanostructured adsorbents can be used to adsorb CO_2 at an acidic pH value to retain the CO_2 gas in the culture and consequently enhance algal growth by controlling the availability of CO_2 in the culture medium through an adsorption/desorption cycle [72].

CO_2 adsorption can be achieved through physical and chemical processes. The physical adsorption of CO_2 on nanostructured adsorbents is affected by the surface area, and pore size and volume. The pore size of adsorbents is responsible for the selectivity of an adsorption process. By considering the size of CO_2 molecules (~0.33 nm), the smaller pore size enhances the CO_2 adsorption rather than oxygen (~0.36 nm) and nitrogen (~0.35 nm) adsorption. Moreover, the CO_2 adsorption capacity and selectivity of adsorbents can be enhanced by adding some heteroatoms such as nitrogen, oxygen, and sulfur to the nanostructured surface to offer basic sites [73]. The presence of ammonium groups and OH ions on the aerogel consisting of quaternized chitosan and polyvinyl alcohol increases its CO_2 sorption capacity up to 0.18 mmol/g. It was also reported that the selectivity of the aerogel towards CO_2 was better than the commercial membranes [74]. Another study showed the impregnation of amine on zeolite improved CO_2 adsorption up to 4.44 mmol/g [75]. Therefore, besides the surface area and porosity of nanostructured adsorbents, their surface chemistry and the existence of specific functional groups can significantly influence their adsorption capacity for CO_2 [72,76].

Recent studies showed that nanostructured adsorbents had higher CO_2 capturing capacity and reusability over several adsorption/desorption cycles than other popular adsorbents. This might be attributed to their high specific surface area and functionality that can provide more accessible adsorption sites for CO_2 [72,76]. Carbonization of pine cone shells at 650 °C and subsequent activation by KOH enhanced the CO_2 adsorption capacity up to 7.63 mmol g^{-1} and 2.35 mmol g^{-1} at 0 °C under 1 and 0.15 bar pressure, respectively, due to increasing specific surface area and porosity [77]. Several studies reported the promising performance of polyacrylonitrile (PAN) nanofiber in adsorbing and supplying CO_2 for microalgae cultivation [76,78,79]. The addition of PAN nanofiber at $0.1 \cdot g \cdot L^{-1}$ to the *Chlorella fusca* LEB 111 culture was found to improve biofixation and carbohydrate production by 45% and 2.3%, respectively, compared to the control without the nanofiber [78]. Metal nanoparticles can be added to the nanofiber to further enhance CO_2 biofixation. The addition of iron oxide NPs at 4% w/v to PAN nanofiber significantly enhanced the CO_2 fixation in *Chlorella fusca* LEB 111 to 216.2 $mg \cdot L^{-1} \cdot d^{-1}$ due to the high CO_2 adsorption capacity of Fe_2O_3 NPs (164.2$\cdot mg \cdot g^{-1}$), increasing the contact time between gas and microorganisms by enhancing the porosity and providing higher surface area [79] and creating the microorganism–nanoparticle hybrid [80].

4.3. Nanoparticles for Improving Light Harvesting and Usage Efficiency in Algal Photosynthesis

Although the theoretical maximum efficiency of microalgae photosynthesis of converting sunlight to biomass is around 13%, only half of that value can be achieved because of insufficient illumination and nutrients, and wasted illuminating. Wasted illumination is described as inhibiting algae growth under extra illumination due to the radiation damage and toxic stress via the accumulation of reactive oxygen species. The problem of wasted illumination can be addressed by optimizing the photobioreactor parameters such as geometry shape and homogeneity of the algae culture, genetic modification of algae to increase the antenna size, and adjusting the photopigment accumulation. Research showed that there was a direct relationship between illumination and pigment accumulation in photosynthetic organisms. The main photopigments in microalgae are chlorophylls and carotenoids. Chlorophyll photopigments consist of *chlorophyll a* and *chlorophyll b* that are located within the reaction centers of photosystem I and photosystem II, and antenna complex, respectively. The main light absorption of chlorophyll photopigments occurs at 410–430 nm and 660 nm for *chlorophyll a*, and 450 and 640 nm for *chlorophyll b*. The light absorption wavelength of carotenoids is between 400 and 500 nm which is outside of the chlorophyll wavelength ranges [81].

The removal of lights in the unwanted wavelength regions can mitigate the insufficient and wasted illumination and subsequently enhance the chlorophyll content of green algae. Study showed that the replacement of white light with blue light enhanced the chlorophyll formation in algae [81]. Some light at specific wavelengths and optimum intensity can be used by photoactive pigments in algae while other light is a photoinhibitor to the algae. Therefore, the filtration of light by intensifying the useful light with specific wavelengths and removing the photoinhibitor light can significantly improve the photosynthesis efficiency and algal biomass yield. As shown by Torkamani et al., the photoactivity and growth of *Chlamydomonas reinhardtii* (green alga) and *Cyanothece* 51142 (green-blue alga) were increased by adding silver nanoparticles to filter the absorbed light under the localizing surface plasmon resonance (LSPR) [82]. The LSPR technique can be used to filter light with certain wavelengths through the interaction between the electric field of the light and the conduction band of electrons of metal nanoparticles. The LSPR technique can create a light with a tunable narrow scattering wavelength by controlling the geometry and composition of metal nanoparticles [81]. In this way, changing the size, shape, and concentration of the nanomaterials can tune the frequency of the scattered light and eliminate the photoinhibition light by controlling the scattered light flux [82]. As demonstrated by Eroglu et al., the LSPR using spherical silver nanoparticles and gold nanorods can enhance the *Chlorella vulgaris* growth by filtering the backscattered light to violet-blue and red regions, respectively [81].

Another advantage of using nanoparticles in an algal culture medium is to create the uniform distribution of light to algae cells. Study showed that the addition of silica nanoparticles could enhance the chlorophyll content and subsequent growth of *Chlamydomonas reinhardtii* through uniform illumination to algae cells [83]. Nanoparticles can be used to redistribute the local intense incident light in a culture through their fluid nature in the culture, allowing flexible and deficient backscattering [63].

4.4. Nanoparticles for Improvement on Algae Harvesting

Harvesting technology is crucial for the commercial production of microalgae. The selection of an algae harvesting method is highly dependent on several factors: the physiognomic structure, cell density, algal size, final moisture content, and the reusability of the culture medium [84]. Conventional harvesting technologies include centrifugation, flocculation by coagulants, precipitation by pH increment, filtration, and flotation [85]. Magnetophoretic harvesting by tagging algal cells with magnetic particles and then separating them from the culture medium by an external magnetic field has emerged as an energy-efficient and time-saving technology for microalgal harvesting [86]. Fe_3O_4 NPs are commonly used due to their high specific surface area, superparamagnetism and biocompatibility. However, tagging magnetic Fe_3O_4 NPs to the negatively charged algal cells requires a specific pH range at which zeta potential of magnetic nanoparticles shows positively charged surface. As a result, the coating of cationic materials onto Fe_3O_4 NPs is needed. These cationic materials are normally polymers such as polyethylenimine and polyamidoamine (PAMAM) [87,88]. As reported by Hu et al., 20 mg/L of Fe_3O_4–polyethylenimine nanocomposite enhanced the harvesting efficiency and adsorption capacity of the *Chlorella eppipsoidea* by 97% and 93.46 g dry microalgal cell weight/ g nanocomposite, respectively [89]. The impact of amino acids on improving the harvesting performance of Fe_3O_4 has been studied. It was shown Fe_3O_4 @ arginine nanoparticles could enhance the harvesting efficiency of *Chlorella* sp. cells by 95% at a dosage of 200 mg/L. The number of amine groups in amino acid molecules and the amino acid content of nanoparticles significantly affect the harvesting performance [90].

5. Nanomaterials for Microbial Fuel Cells

Microbial fuel cells (MFCs) as shown in Figure 2 [91] are bioelectrochemical systems that can generate electricity from the organic substances in wastewater using proper microbial. Electrogenic microorganisms break down organic matters in the electrolyte to produce carbon dioxide, hydrogen ions, and electrons in the anode. Electrons are then transferred along the outer circuit to the cathode, and hydrogen ions diffuse to the cathode through the solution. In the cathode, the oxidant is reduced by the hydrogen ions and electrons. Electrical current is thus produced in such a close loop. Various efficient, cost-effective and eco-friendly nanomaterials have been developed as catalysts, membranes and adsorbents to enhance the performance of MFCs. Agrahari et al. provided a review on the recent development of electrode materials for MFCs [92].

5.1. Nanostructured Bioelectrodes

An MFC requires anode and cathode electrodes. Biofilms on the anode electrode oxidize biodegradable organic matters in wastes to liberate electrons and protons. Protons and electrons from an anode will be combined with oxygen at the cathode electrode to produce water. The electrodes should have high surface area and excellent abilities in extracellular electron transport and electrical conductivity to achieve high power density.

Colonization of microorganisms requires anodes with a high porosity, proper pore size, biocompatibility, low cytotoxicity, and resistance to decomposition. Metal components have high conductivity, but their bacterial adhesion is poor. Furthermore, they may be susceptible to corrosion and liberate toxic heavy metals. Carbon-based materials such as graphene and carbon nanotubes provide great surface area facilitating the colonization of microbes, biocompatibility and high conductivity [91]. Nanostructured biocatalyst electrode architectures can be designed and optimized as an excellent MFC anode [93].

One economic and effective way to increase power output of an MFC is to depose of metal or metal oxide (e.g., gold and ruthenium oxide) nanoparticles on the surface of electrodes [94,95]. It was found that carbon cloth-based anode electrodes deposited with Au with a thickness of 50 nm and 100 nm on each side achieved power density 1.22–1.88 times higher than that obtained with a plain carbon cloth electrode [95]. Another study showed that the dual chamber MFC with a RuO_2-coated carbon felt anode increased the power density by 17 times as compared to that obtained with the MFC using a bare carbon felt anode [94].

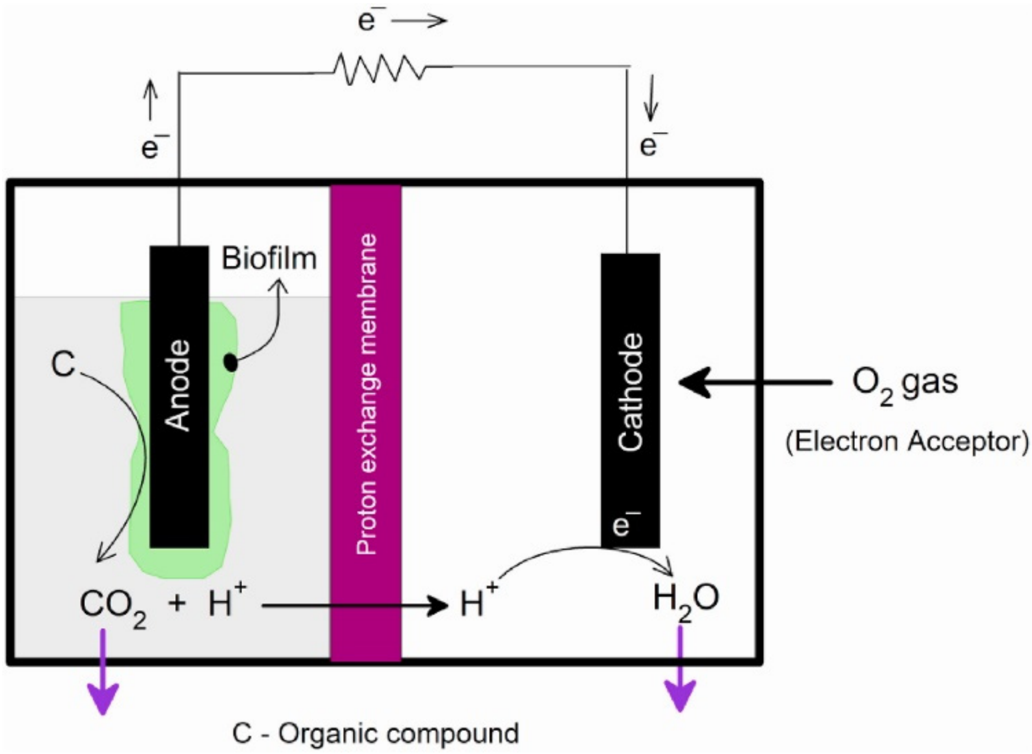

Figure 2. A typical MFC system (reprinted with permission of Elsevier) [91].

Polyaniline that has high electrical conductivity can facilitate the electron transfer from bacteria to external circuit on an MFC anode. Study showed that an anode formed by coating polyaniline nanofiber and electrochemically reducing graphene oxide on the surface of carbon cloth yielded a maximum power density of 1390 mW/m^2, which was three times larger than that of the MFC with a carbon cloth anode [96]. It was reported that an anode formed by a hydrogel composite with bacterial cellulose as a continuous phase and polyaniline as a dispersed phase could achieve a maximum power density of 117.6 mW/m^2 in a current density of 617 mA/m^2, compared to 1 mW/m^2 and 10 mA/m^2 using a graphite plate anode at the same condition [97]. Hydrogel can achieve excellent nutrient transfer from the culture medium to attached microbial biofilm, provide favorable conditions for bacteria colonization, and prevent it from spoilage. Polyaniline with a high electrical conductivity can facilitate the electron transfer from bacteria to external circuit [97].

Various metal and non-mental nano-composites such as carbon nanotubes and graphene have been studied as cathode catalysts [98]. Owing to its availability and the high electrochemical oxygen potential, an air-breathing cathode MFC is considered as the most promising configuration. An air-breathing cathode usually consists of an electrode substrate, oxygen reduction reaction (ORR) catalyst layer, and air-diffusion layer [99]. The air-cathode catalyst is pivotal in the performance of MFCs because of its role in improving the intrinsic overpotential and poor kinetics of ORR. Although exhibiting the best ORR performance, Pt group metals-based electrocatalysts have high cost, low abundance, and easy deactivation in the presence of MFC metabolites, hindering them from broad industrial application. So far, numerous non-noble metal inexpensive electrocatalysts with an excellent catalytic ability such as Fe-N/C catalysts have been studied. Various Fe-N/C catalysts were synthesized to introduce Fe and N as dual-dopants on the carbon so that the catalytic sites, i.e., Fe-Nx and N-Cx, can be generated [100]. The typical synthesis method is to pyrolyze the widely available precursors comprising of iron salts, nitrogen-rich molecules, and carbon precursors under a high temperature in either N_2 or NH_3 environment. The carbon component in the catalysts serves as the conductive support and the host of active moieties.

In general, an ideal electrocatalyst should possess good electrical conductivity, hierarchical pore structure, large specific surface area, and competent active sites. Therefore, the iron-containing precursors are normally introduced in various carbonaceous materials including active carbon, graphene, carbon nanotube (CNT), conducting polymers, and porous carbons. The heteroatoms (Fe and N) can be introduced into the carbon materials by pyrolyzing FePc-coated activated carbon [101]; by co-doping hierarchical porous iron and nitrogen in carbons via coupling polypyrrole with iron cation [102], and by using metal-organic-framework (MOF) of dual metal- and nitrogen-doped carbon as a precursor [103].

5.2. Nanostructured Proton Exchange Membranes

A proton exchange membrane (PEM) that is an ion selective membrane separating cathode and anode compartments of an MFC is also a key component which strongly influences the efficiency and economic viability of the MFC by affecting the transmittance of generated protons in anode compartment to the cathode chamber. A PEM must have a good potential for exchanging protons and mitigating anode electrolyte between anode and cathode compartments of an MFC. Moreover, it must prevent the leakage of air that is used in the cathode chamber into the anode compartment [104].

Different types of materials have been used to make various PEMs including Nafion, Ultres, bipolar membrane, dialyzed, glass wool, microfiltration membrane, polystyrene and divinylbenzene. Among those membranes, Nafion is the most common PEMs used in MFCs. However, Nafion PEMs have several disadvantages including high costs, oxygen leaking from cathode compartment to anode compartment, and higher cations transport and accumulation than protons, which limits their applications [105]. Main obstacles in commercialization of MFCs are the high price of PEMs, low performance, and low power generation. Due to the high price of PEMs, there is a great interest to find an alternative for Nafion PEMs. Power output per unit cost is an important index which must be taken into account for the development of economic PEMs [104].

Several studies showed the use of nanotechnology on improving the performance of PEMs. Ghasemi et al. (2012) reported that nanocomposite membrane of Nafion and activated nanofiber (ACNF/Nafion), and non-activated nano fiber (CNF/Nafion) could produce 1.5 times and 27% more power than the traditional Nafion 117, respectively, by enhancing the conductivity and porosity of the membrane [106]. Moreover, by considering the impact of increasing mass transfer area and decreasing the thickness of membrane on enhancing current and power density, the higher performance of nanostructured membranes can decrease the power output per unit cost and improve the cost effectiveness of the MFCs [104].

When protons are transferred from anode to cathode through a PEM, another challenge is attributed to the competition between protons and other cations in reacting with negatively charged functional groups on the PEM. The combination of non-proton cations stops the movement of protons from anode to the cathode chambers [104]. Due to the great potentials of polymer/inorganic nanomaterials in various aspects of science, there is a great attention for their application in membrane fabrication [105]. The distribution of nanoparticles through a polymer matrix can modify the physicochemical properties of the polymer to generate selective permeation paths for mitigating the movement of undesirable materials, and improve its mechanical and thermal properties as well [104,105,107]. Iron NPs, especially in the form of Fe_3O_4 have gained considerable attention because of their high electric conductivity, ease of fabrication, and eco-friendliness. Study showed that the composite of Fe_3O_4 NPs and polyethersulfone was a promising cost-effective alternative PEM to an Nafion PEM by enhancing the power and current density by 29.9% and 32.1%, respectively, due to its high proton transferring capability [105].

6. Perspectives and Conclusions

The increasing population, and rapid urbanization and industrialization have resulted in a tremendous increase in biowastes which must be recycled and valorized to reduce their disposal cost and land usage and mitigate their negative impacts on human health and the environment. Moreover, the high population growth and dependency on fossil fuels cause the depletion of natural resources and negative environmental impacts. The conversion of biowastes to energy and other value-added products can simultaneously solve the waste disposal problem, decrease fossil fuel usage, and mitigate their negative environmental impacts. Innovative conversion technologies for the valorization of agricultural wastes are crucial in the circular economy and the transition to sustainable agriculture. Integrating biowaste management into a circular economy can increase the economic efficiency of natural resources and environmental sustainability.

AD, microalgae cultivation, and MFCs have been considered as three promising biological processes for transforming agricultural wastes into value-added products such as biofuels, biochemicals, and biopower. AD, microalgae cultivation, and MFCs use microbial and microalgae as cellular factories for simultaneous production of bioenergy products and treatment of agricultural solid wastes and wastewater. However, those bioconversion processes suffer the low conversion efficiency, low productivity, and poor stability. Various nanomaterials have been studied to improve the efficiencies of microbial and microalgal cell factories in AD, microalgae cultivators, and MFCs by providing micronutrients, promoting multiple phase mass transfer, promoting electron transfer in electro-synthesis, preventing sulfur/ammonium inhibition, immobilizing microbial cells, and efficiently and economically harvesting cells.

Nanomaterials with nano-sized structures and specific physicochemical properties can have positive and negative effects on the performance of microbial and microalgae, depending on the type of nanomaterials and their concentrations. Furthermore, the effectiveness of nano-additives on the enhancement of the performance of AD, microalgae, and MFCs strongly depends on their formulation, dosages, size, process conditions, and type of feedstocks. The studies reported in literature were mostly focused on the use of nanomaterials for the enhancement of a specific single function of the AD, microalgae cultivation and MFCs such as micronutrient supply and inhibitor removal. More studies are needed to manufacture, characterize and test multifunctional nanocomposite materials that can effectively enhance the performance of AD, microalgae, and MFCs from various aspects. Another main challenge for the wide use of nanomaterials in the waste–biorefinery processes is the high cost of nanomaterials. It is thus necessary to develop bio-compatible and cost-effective nanomaterials to expand their industrial applications at a large scale. Due to the small size of nanomaterials, it is difficult or economically impossible to recycle the nanomaterials added to AD, microalgae culture, and MFCs. Therefore, besides the technical challenges to develop proper nanomaterials for the enhancement of the performance of the waste–bioconversion processes, the potential issues of biosafety, negative environmental impacts, and downstream processes associated with the applications of nanomaterials should also be studied.

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