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Review

Recent Advances and Perspectives of Nanotechnology in Anaerobic Digestion: A New Paradigm towards Sludge Biodegradability

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Abstract: Anaerobic digestion (AD) is the strategy of producing environmentally sustainable bioenergy from waste-activated sludge (WAS), but its efficiency was hindered by low biodegradability. Hence, the usage of nanomaterials was found to be essential in enhancing the degradability of sludge due to its nanostructure with specific physiochemical properties. The application of nanomaterials in sludge digestion was thoroughly reviewed. This review focused on the impact of nanomaterials such as metallic nanoparticles, metal oxide nanoparticles, carbon-based nanomaterials, and nanocomposite materials in AD enhancement, along with the pros and cons. Most of the studies detailed that the addition of an adequate dosage of nanomaterial has a good effect on microbial activity. The environmental and economic impact of the AD enhancement process is also detailed, but there are still many existing challenges when it comes to designing an efficient, cost-effective AD digester. Hence, proper investigation is highly necessary to assess the potency of utilizing the nanomaterials in enhancing AD under various conditions.

Keywords: anaerobic digestion; biogas; cost; environmental impact; nanomaterial; waste-activated sludge

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1. Introduction

The increased population relies on energy for survival and destroys environmental resources, which creates issues such as ecological imbalance, global warming, etc. Energy is a resource vital to the wealth of a nation that determines the economy of a country [1]. Globally, 88% of energy is obtained from fossil fuels, which leads to greenhouse gas emissions. This harmful effect of fossil fuel makes it unfit and initiates the usage of waste biomass to generate nonconventional energy [2]. Bioenergy currently provides roughly 10% of global supplies and accounts for roughly 80% of the energy derived from renewable sources. Bioenergy was the main source of power and heat prior to the industrial revolution. Since then, economic development has largely relied on fossil fuels. A major impetus for the development of bioenergy has been the search for alternatives to fossil fuels, particularly those used in transportation. Thus, bioenergy production is considered a better option for societal concerns. Waste-activated sludge-derived bioenergy has numerous diverse benefits and can be used as fuel, electricity, etc. An eminent environmentally sustainable method of producing energy from sludge is anaerobic digestion (AD) [3]. AD is a microbial biological conversion method that converts an organic fraction of the waste biomass to bioenergy in the form of biogas without the presence of oxygen. It consists of four phases of reaction: hydrolysis, acetogenesis, acidogenesis, and methanogenesis, which are provided in Figure 1.

Organic fractions that exist in waste biomass have a complex structure with different characteristics and properties that lead to technical challenges during AD [4]. Complex structured organic biomass such as sludge consists of an extracellular polymeric substance (EPS) layer that affects microbial hydrolysis by hindering the substate accessibility [5]. This affects the sludge biodegradability. In the case of readily degradable waste biomass, namely food waste, the rate of hydrolysis and acetogenesis increases more than the methanogenesis phase. This results in the accumulation of volatile fatty acids (VFA) [6,7]. To overcome these two issues, remedial processes such as pretreatment [8], co-digestion [9], the addition of additives [10], etc., are highly preferred. Researchers detected an increase in the amount of NPs usage in biodegradable waste as a result of increased use of certain additives in key industries. This prompted an examination of the possible consequences of waste-activated sludge (WAS) on AD and its impact on different metallic and metal oxide NPs. Initial research revealed that some NPs (e.g., Ag and TiO_2) at certain dosages have no adverse impact on AD in terms of biogas and methane output, as well as the proportion of microbes implicated in AD and its diversity, while others (Au, CeO_2) may have a detrimental effect on this process. However, bulk material additives are not biodegradable during the AD process, and high concentrations of bulk material can lead to toxicity and microbial inhibition.

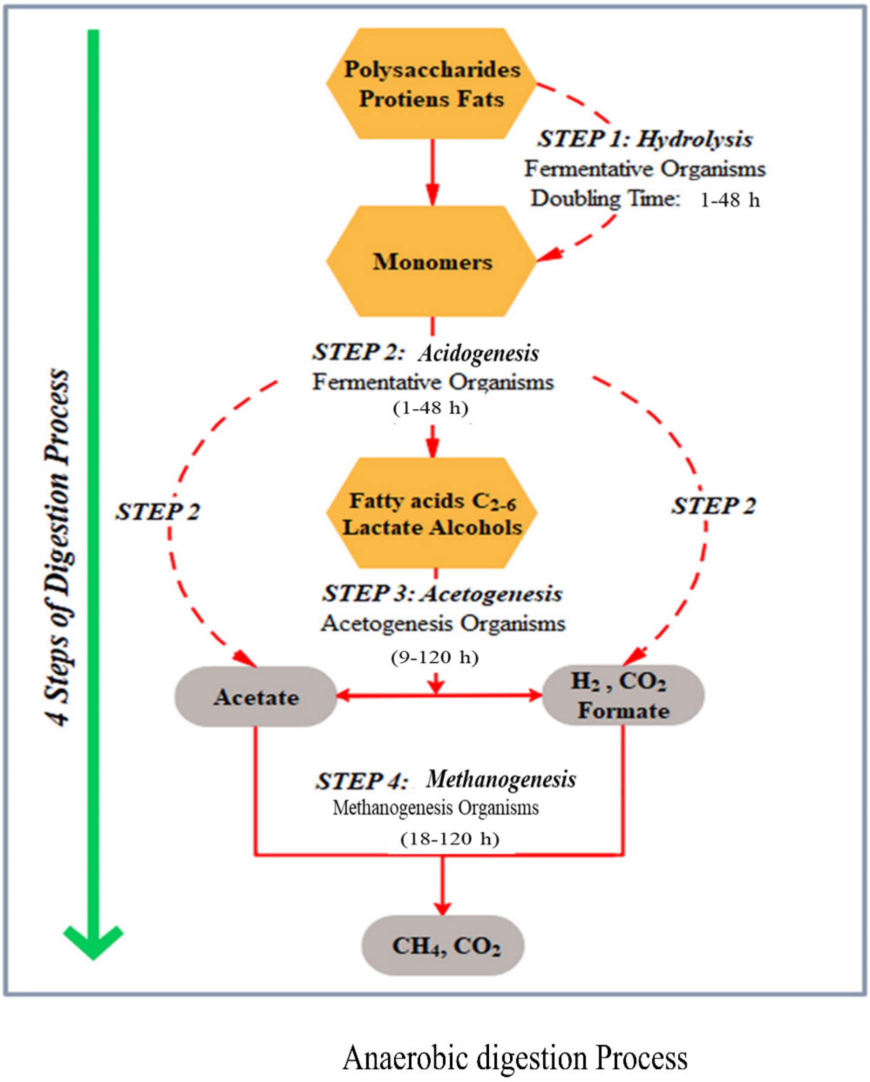

Figure 1. Various steps are involved in the anaerobic digestion process [7,8].

In addition to this, innovative approaches have been formulated which were mainly focused on advancing the AD process to create new energy production techniques with more financial benefits. The economic viability of the large-scale NPs-augmented AD process is mainly dependent on the price of NPs. Moreover, regardless of the economic feasibility issue, the application of NPs in any industry (including the biogas industry) raises some environmental risks that must be appropriately addressed. Meanwhile, the objective of this review is to provide insights into various nanoparticles in the AD process in terms of gas yield, effluent quality, as well as their influences on fundamental mechanisms. Additionally, it addresses the environmental and economic impact of NPs during AD. Finally, the research requirements in this area have been reviewed, and the suggested perspectives have been listed.

2. Various Nanomaterials in AD Enhancement

Enhancement of AD using nanomaterial to augment the biogas yield has received great consideration in the field of research due to its distinct physical properties such as increased surface area and structure, particle size, catalytic activity, etc. [11]. The nanoparticles (NPs) movement was prompted by direct interspecies electron transfer within the anaerobic environment to enhance the methane-generation rate [12]. These nanomaterials can penetrate the cell membrane of the microbial cell, thereby reducing the lag phase to enrich the methane formation. Various types of nanomaterial are utilized to enhance the AD and the % of the usage was given in Figure 2.

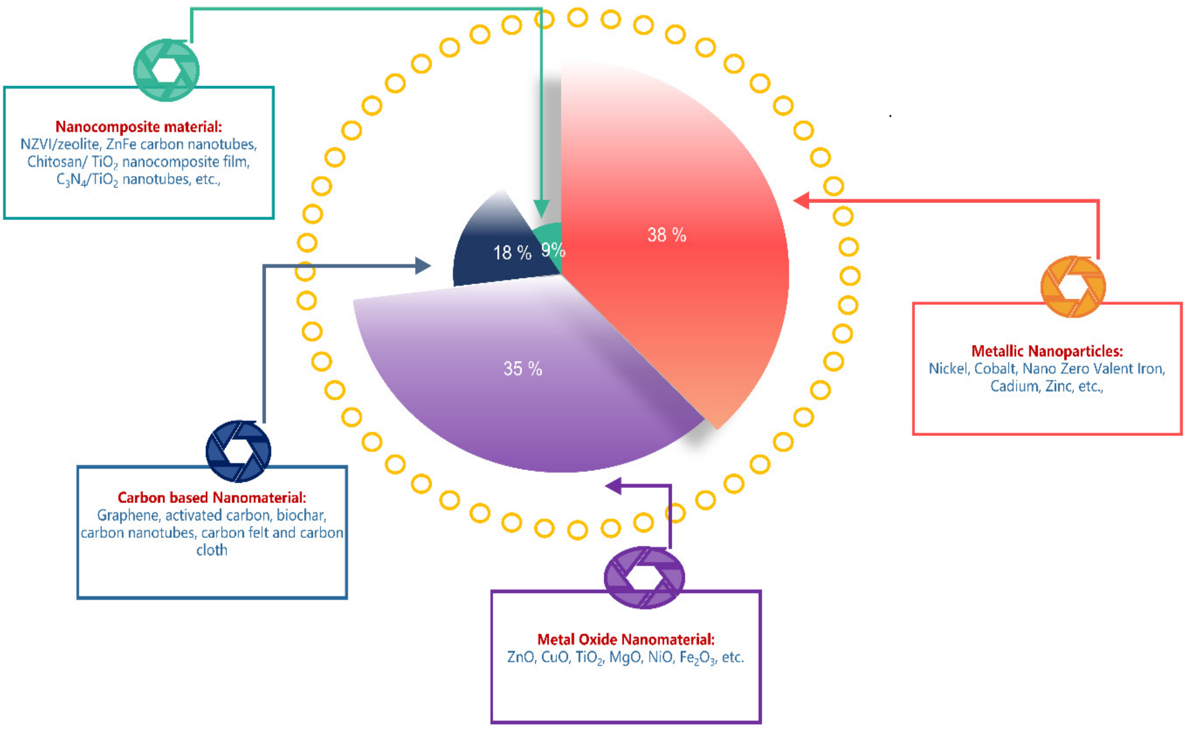

Figure 2. Types of various nanomaterials and its percentage of usage in AD.

2.1. Metallic Nanoparticles

The addition of metallic nanoparticles (such as Nickel (Ni), Copper (Cu), Silver (Ag), Cobalt (Co), and Gold (Au)) in the AD process enhances its performance by reducing the lag time, resulting in increased methane generation [13]. These metal compounds are considered a trace element for enhancing AD, and act as a co-factor for many key enzymes which are essential for the growth of the microbes, such as *Methanosarcina barkeri*; *Methanospirillum hungatii*; *Methanocorpusculum parvum*; *Methanobacterium thermoautotrophicum* and *Methanococcus voltae*; *Methanococcus vanielli*; and *Methanococcoides methylutens* at various stages of AD [14]. It functions as a major source of initiators, assists in the production of essential enzymes and co-enzymes, and accelerates anaerobic microbial function at optimal concentrations.

Because of its effective role in the active site of the methyl co-enzyme M reductase, Ni nanometal is considered essential for the methane fermentation. Nearly 2.3 to 4.8 μg/g of CODfed is required for the effective acidogenic pathway [15]. Khan et al. [16] observed that adding 4 mg/L of Ni improved the biogas yield to 308.33 mL/d at 23rd day. Abdelsalam et al. [17] yielded 2.01 times increased methane output of 316.6 CH_4/g VS from slurry digestion compared to the control sample on addition of 2 mg/L of Ni nanoparticle. On addition of Ni nanoparticle to the cattle dung digestion, 70.46% increased methane output was achieved with a 90.47% decrement in hydrogen sulfide gas. In addition, 19.2% and 12.1% of total suspended solid (TSS) and volatile suspended solids (VSS) removal was obtained at pH Level of 6.8–7.3 with 1.88-fold increment in the hydrolysis rate constant [18]. Ni nanometal of concentrations ranging from 0.5 to 2 mg/L enhanced the AD of dairy manure by 55–101%. Zaidi et al. (2019) pretreated the sludge using a 600 W microwave for 6 min and carried AD with Ni nanometal additives (0.16 mg/g TSS) enhanced 31.73% of methane generation [19].

Cobalt served as a conductive enzyme activator, contributing to the inhibition of the metabolism more than a certain threshold. Sludge exhibited great biomethane production up to 0.02 mg/L and a slight decline after 0.05 mg/L. The sludge-based biomethane production showed poor metal toxic effects tolerance and was able to restore substantially with a cobalt-level increment [20]. The Cobalt (Co) metallic nanoparticle also fostered the performance of the AD at various concentrations up to 1 mg/L and enhanced the methane production of 41.9% in poultry litter. Beyond the threshold concentration, it acts as an inhibitor, affecting the digestion process. Next, 1 mg/L of Co enhanced the methane yield twice the times than the control sample. Additionally, mild toxicity of 12.7% was reported when Co concentration increased to 2 mg/L [21]. Addition of 0.16 mg/g TSS Co during AD of microwave pretreated sludge sample enhanced 42% of biogas production. (Zaidi et al., 2019). Digesting the raw manure using 1 mg/L of Co (size—28 nm) enhanced 45.92% of biogas generation [17]

Copper (Cu) is an enzymatic activator with less toxicity which chelates other substances and reduces other metal toxicity. The sludge with 4.5 mg/L of Cu concentration produced a high amount of biomethane. A decline in biomethane generation was detected above 5 mg/L of Co concentration. Resulting in a high proportion of microbes and nutrients for metabolic activities, sludge holds the responsibility for methane production [22]. The concentration that prevents the digested sludge from being produced was found to be 15 mg/L. It was caused by microbes accumulating excessive amounts of trace metals over the threshold. The AD copper concentration threshold was 40 mg/L, according to Matheri et al. [23] and Bozym et al. [24]

The Ag nanoparticle showed an inhibition effect on sludge during AD. Additionally, 500 mg/g of Ag inhibited 27% of biogas production during sludge digestion. The reason for this reduction is that a high concentration of Ag nanoparticles damages the cell membrane and reduces the total nitrogen level [25]. Similarly, about 12.1% of methane reduction was observed in the digestion of sludge when 5–1000 mg/g TS of Ag was added. In the case of the granular sludge, no toxic effects on the methanogenic activity were found following addition of a dosage of 1500 mg/L of Ag in the batch digester.

Trace element combinations have significant synergistic effects [5]. Enhanced Ni and Co dosages might ramp up initial exponential rates and augment the methane volume and methanogen cell densities [26]. This enhanced methane generation is due to increased transcription of mcrA (the gene coding for the alpha subunit of methyl-coenzyme M reductase), which alters methanogenic consortium dynamics and boosts methanogenic activity. Additionally, Ni has potential interaction with Cu, Mo, Co, and Hg, as well as adverse interactions with Zn and Cd. Cd^{2+} can enhance methane production and facilitate the productivity of *Methanosarcina acetivorans*. Cd, when coupled to other metals, boosted biogas generation as well as enhancing CH_4 content. The addition of Zn to the AD system reduced Cd toxicity while increasing biogas output [27]. The methods through which Zn and Cd enhance the AD process remain uncertain.

In the domain of biogas generation, NZVI (Nano Zero valent Iron) has been extensively researched as a nanoscale zero valent metallic addition. When utilized as a reductive material, zero valent iron (ZVI) may diminish oxidative reductive potential in anaerobic systems, offering a more suitable environment for anaerobic metabolic processes, which was detailed in Figure 3 [28]. ZVI was found to have beneficial effects on AD, including H_2S elimination, activation of important enzymes in the acidification process and methanogenesis, and lowering of oxidation-reduction potential (ORP) [29,30]. A low ORP environment may be beneficial to AD. ZVI with high reaction conditions can directly interact on contaminants [31,32]. This entails the controlled transport of electrons. The electrons produced by ZVI are transferred to pollutants, transforming it into less toxic or nonpoisonous compounds. The electrons produced by ZVI corrosion in the ecosystem stimulate the metabolic processes of microorganisms. It can create H_2O_2 by transferring electrons into O_2 via dissolved oxygen. Fe^{2+} reacts with H_2O_2 to form •OH, which has a high oxidation capacity. Because of its role as an electron donor, ZVI can be used to promote a range of alternative enzymatic functions in acidification and boost methanogenesis. Suanon et al. [33] added 100 mg/L nZVI that was 160 nm in size to the batch bio-digester during the AD of sewage sludge, which increased methane generation up to 25.2%. Similarly, the enhancement of 30.4% of biogas and 40.4% of methane was observed in sewage sludge when 10 mg/L of nZVI was added to the AD process on the 17th day [34]. The observations were consistent with studies conducted previously. Addition of 10 mg/g TSS NZVI to the waste-activated sludge (WAS) improved 120% of methane production. Amen et al. [35] achieved 105.46% of methane enhancement when 1000 mg/L of NZVI was added to the sewage sludge. Increased trace metals in the digestate can hinder AD function. Determining the ideal levels of heavy metals for every AD system is meant to encourage the advancement of sustained clean-energy sources [36,37]. Table 1 provides the various nanometal additives involved in the enhancement of anaerobic digestion.

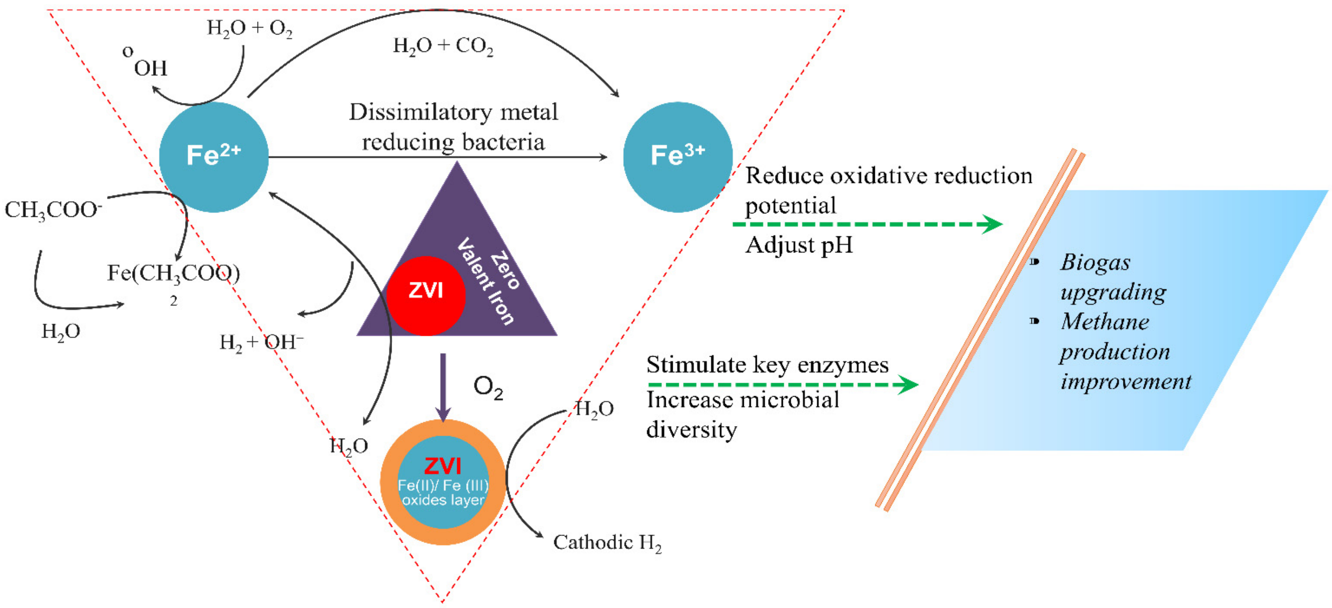

Figure 3. Mechanism behind the nano zerovalent iron in enhancing AD.

Table 1. Various metallic nanoparticles involved in AD enhancement.

S.No	Metallic Nanoparticle	Substrate	Nanoparticle Dosage	Size	Reactor Used	Impact on Methane Generation	References
1.	Ni	Sewage sludge	5–10 mg/KgVS	100 nm	Batch and CSTR	10% increment	[29]
2.	Cu	Granular sludge	10–1500 mg/L	40–60 nm	Batch	Inhibition	[30]
3.	Co	Manure slurry	1 mg/L	28 nm	Batch	86% increment	[17,31]

Table 1. *Cont.*

S.No	Metallic Nanoparticle	Substrate	Nanoparticle Dosage	Size	Reactor Used	Impact on Methane Generation	References
4.	NZVI	Waste-activated sludge	10 mg/g TSS	128 nm	Batch	120% increment	[32]
5.	NZVI	Sewage sludge	100 mg/L	160 nm	Batch	25.2% increment	[33]
6.	NZVI	Sewage sludge	10 mg/L	20 nm	Batch	40.4% increment	[34]
7.	NZVI	Domestic sludge	1000 mg/L	45 nm	Batch	105.46% increment	[35]
8.	NZVI	Digested sludge	56,560, and 1680 mg/L	55 nm	Batch	20% decreament	[36]
9.	NZVI	Granular sludge	1500 mg/L	46–60 nm	Batch	No inibition	[30]
10.	Ag	Waste-activated sludge	500 mg/g TSS	170 nm	Batch	27% decrement	[25]
11.	Ag	Biosolid from wastewater treatment plant	0.5, 1, 5 and 100 mg/L	10–15 nm cationic silver NPs	Batch	Complete inhibition	[37]
12.	Ag	Municipal waste-activated sludge	5–1000 mg/gTS	20–40 nm	Batch	12.1% decrement	[38]
13.	Ag	Granular sludge	1500 mg/L	<100 nm	Batch	No inhibition	[30]

2.2. Metal Oxide Nanomaterial

Metal oxide NPs are essential in various fields of chemistry, physics, and materials science. Because of their tiny size and high density or edge-surface sites, metal oxide NPs can have unusual physical and chemical characteristics. Metal oxide NPs are available in a multitude of forms, including Titanium dioxide (TiO_2), Zinc Oxide (ZnO), Magnesium Oxide (MgO), Nickel Oxide (NiO), Ferrous oxide (Fe_2O_3), Cuppor Oxide (CuO) nanoparticles, and so on [39]. Metal oxide NPs are being used in the biogas generation process, mostly in the growing nanotechnology field. Hence, the impact of metal oxide nanomaterial on AD efficiency was assessed by various researchers from this perspective.

TiO_2 is quite cheap compared to other nanomaterials and has strong thermal and chemical stability, as well as minimal toxicity in humans [40]. It is generally utilized in treating wastewater and antibiofouling due to its photocatalytic capabilities. The fundamental benefit of TiO_2 nanoparticles is that they have an infinite lifetime and may not degrade when exposed to bacteria or chemical molecules. Iron oxide nanoparticles have been frequently employed to remove heavy metals in the past decade due to their easy usage and accessibility. Enhanced characteristics, a large surface area, high tensile strength, and low particle size are all advantages of iron-oxide-based nanomaterials [41]. Nano adsorbents include magnetic magnetite (Fe_3O_4), nonmagnetic hematite (Fe_2O_3), and magnetic maghemite (Fe_2O_4). The major hurdles of using nano adsorbent in sludge management are their small particle size, difficulty in separation, and recovery from the sludge. However, the metal oxide NP (Fe_3O_4 and Fe_2O_4) was the opposite of nano adsorbent, since it can be easily recovered and separated after the treatment process. A monoclinically organized structural semiconductor copper (II) oxide contains a number of beneficial chemical and physical properties, such as solar energy efficiency, superconductivity at high temperatures, and relative stability, which are cheap in cost with improved antibacterial activity [42]. Copper oxide nanomaterial research has blossomed in the last year due to its tremendous compatibility, limited fabrication, and good electrochemical characteristics. ZnO is the earliest and most extensively used material for heterogeneous photocatalysis. Due to its unique feature, ZnO is considered a highly potent catalyst for wastewater remediation [43].

These characteristics include low cost, abundance, and non-toxicity. Among other metal oxides, Silver oxide (Ag_2O) nanoparticles are metallic oxides with a high surface area and alluring nanostructures, which are spherical or faceted. Additionally, this Ag_2O nanoparticle has ultra-high purity, and transparent nature. It is available in coated and dispersed forms [44]. These nanoparticles have strong antibacterial action, which is investigated and employed in a variety of commercial goods. Table 2 elucidates the metal oxide NPs enhancing methane generation.

Table 2. Various metal oxide nanoparticles involved in the AD enhancement.

S.No	Metal Oxide Nanoparticle	Substrate	Nanoparticle Dosage	Size	Reactor Used and Volume	Impact on Methane Generation	References
1.	Mn_2O_3	Granular sludge	1500 mg/L	100 nm	Batch 5 L	No Inhibition	[30]
2.	Fe_2O_3	Waste-activated sludge	100 mg/g TSS	128 nm	Batch 500 mL	117% increment	[25]
3.	Fe_2O_3	Granular sludge	750 mg/L	-	Batch 5 L	38% increment	[44]
4.	Fe_2O_3	Granular sludge	1500 mg/L	40 nm	Batch 2 L	No Inhibition	[30]
5.	Al_2O_3	Granular sludge	1500 mg/L	<50 nm	Batch 5 L	25.2% increment	[30]
6.	MgO	Waste-activated sludge	500 mg/g TSS	154 nm	Batch 500 mL	40.4% increment	[25]
7.	CuO	Municipal waste-activated sludge	11, 110, 330, 550, and 1100 mg/L	30–50	Batch 1 L	105.46% increment	[38]
8.	CuO	Granular sludge	10–1500 mg/L	40 nm	Batch 5 L	inhibition	[30]
9.	CeO_2	Sludge	100, 500, 1000 mg/L	-	Batch 3 L	35% inhibiton	[45]
10.	CeO_2	Municipal waste-activated sludge	11, 110, 330, 550, and 1100 mg/L	15–30 nm	Batch 1 L	9.2% increment	[38]
11.	CeO_2	Granular sludge	1500 mg/L	50 nm	Batch 5 L	No inhibition	[30]
12.	ZnO	Waste-activated sludge	10, 300, 1500 mg/L	140 nm	Batch 500 mL	75.1% inhibition	[46]
13.	ZnO	Waste-activated sludge	5, 50, 100, 250 and 500 mg/L	145 nm	Batch 500 mL	50% decrement	[47]
14.	ZnO	Mixed primary and excess	42, 210, 1050 mg/L	120–140 nm	Batch 1 L	High inhibition	[48]
15.	ZnO	Sludge	100, 500, 1000 mg/L	-	Batch 3 L	65.3% decrement	[45]
16.	ZnO	Granular sludge	10–1500 mg/L	10–30 nm	Batch 5 L	High inhibition	[30]
17.	SiO_2	Granular sludge	1500 mg/L	10–20 nm	Batch 5 L	No inhibition	[30]
18.	TiO_2	Mixed primary and excess sludge	42, 210, 1050 mg/L	150–170	Batch 1 L	No inhibition	[48]
19.	TiO_2	Granular sludge	1500 mg/L	25 nm	Batch 5 L	No inhibition	[30]

The effects of inorganic oxide NPs (Copper oxide CuO, Titanium dioxide TiO_2, Zinc oxide ZnO, Cerium dioxide (CeO_2), Aluminum oxide Al_2O_3, iron oxide Fe_2O_3, Silicon dioxide SiO_2, Manganese oxide Mn_2O_3) on acetoclastic and hydrogenotrophic methanogenic activities was studied by Gonzalez-Estrella et al. [30] in granular sludge AD. CuO and ZnO NPs were shown to be strongly inhibitory of the activity of acetoclastic and hydrogenotrophic methanogens. CuO NPs at 62 and 68 mg/L, and ZnO NPs at 87 and 250 mg/L, respectively, inhibited acetoclastic and hydrogenotrophic methanogens by 50%. Corrosion and disintegration of the NPs release poisonous Cu^{2+} and Zn^{2+} ions, which inhibits the process. Methanogens, on the other hand, were not inhibited by high concentrations of CuO, TiO_2, ZnO, CeO_2, Al_2O_3, Fe_2O_3, SiO_2, and Mn_2O_3 NPs, implying that a notable high NPs tolerance was found in anaerobic treatment. Some of the tolerable limits of the metal oxide nanoparticles are provided in Figure 4.

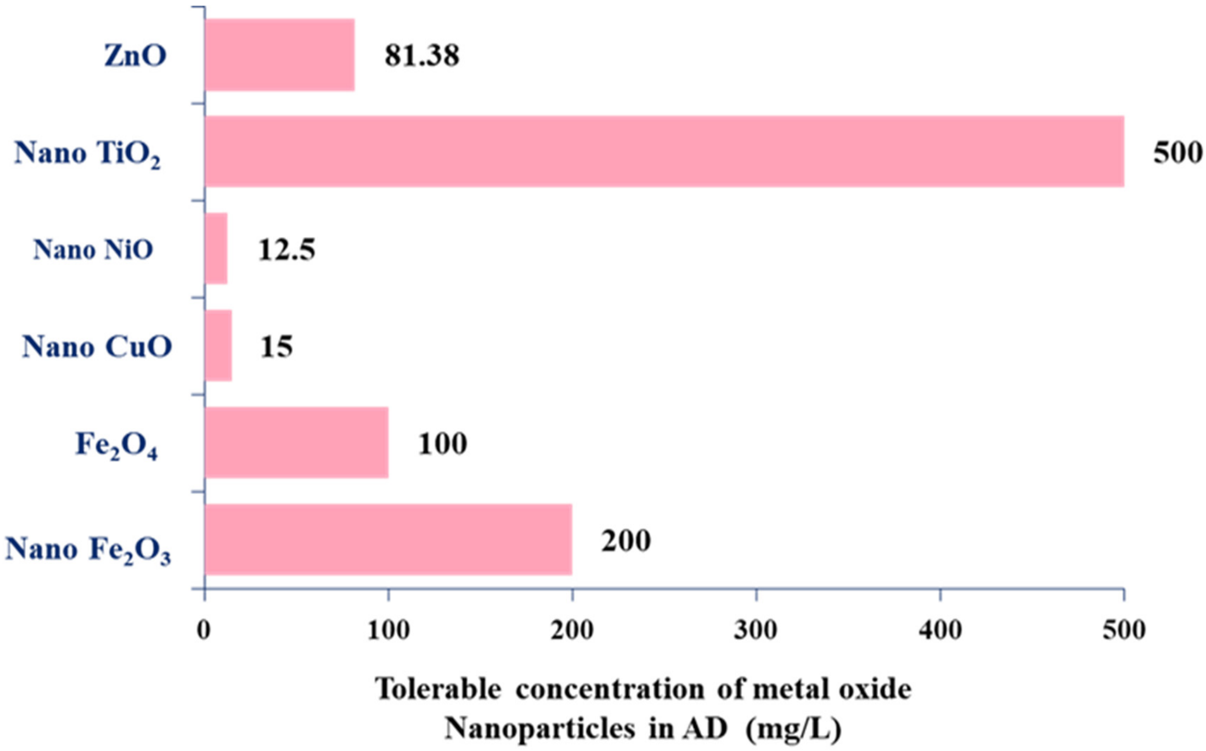

Figure 4. Plot details the tolerable limit of metal oxide NPs usage in AD.

At doses of 6, 30, and 150 mg/g TSS, Mu et al. [46] investigated the effect of TiO_2, SiO_2, Al_2O_3, and ZnO NPs on the anaerobic digestion of WAS. They discovered that adding TiO_2, SiO_2, and Al_2O_3 at various concentrations, as well as adding 6 mg/g TSS ZnO NPs, had no effect on methane generation. However, when 30 and 150 mg/g TSS ZnO NPs were added, it dropped to 77.2% and 18.9%, respectively, supporting prior results. The study found that none of the additional nanomaterials influenced the solubilization process, whereas large doses of ZnO only affected hydrolysis, acidogenesis, and methanogenesis. The biogas production rate declination was associated with the released Zn^{2+} ions from ZnO, according to the study.

The impact of iron oxide nanoparticles (Fe_2O_3) on improving the AD performance of granular activated sludge was explored by Ambuchi et al. [44]. In this study, Fe_2O_3 NPs at a concentration of 750 mg/L generated quicker substrate consumption and biogas generation rates than the control condition, according to the findings. Microbial community research suggested the function of *Anaerolineaceae* and *Longilinea bacteria*, the two most common bacterial genera that are available for the biodegradation process. This might have been raised by NPs utilized in the treatment process. According to Zhang et al. [47], adding ZnO nanoparticles to activated sludge during AD boosted the accumulation of VFAs. The slower generation and consumption rates of VFAs throughout the AD process resulted in increased VFAs accumulation in the presence of ZnO nanoparticles. The suppression of protein hydrolysis by Zn^{2+} ions was a major contributor to the reduction in the VFA generation rate. The reduction in biogas and methane generation was consistent with Mu and Chen's [46] observations, which demonstrated the slow metabolism of VFAs in the presence of ZnO nanoparticles.

Addition of CuO and CeO_2 NPs to enhance AD of WAS showed inhibition in both short-term and long-term exposures [48]. Compared to CeO_2, CuO NPs were the most hazardous to microorganisms during AD. CeO_2 NPs had no profound impacts on the AD process, according to research findings, but exposing 1100 mg/L CeO_2 NPs in the long term resulted in a 9.2% increase in the methane generation rate. On the other hand, CuO NPs concentrations increased the rate of inhibition values from 5.8 to 84.0% when its dosage varied from 11 to 1100 mg/L during AD. Moreover, the hydrolysis rate constant (k_H) of WAS was 0.0277 d^{-1} in all CeO_2 NPs experiments, but it was 0.0016 d^{-1} in high concentrations of CuO NPs.

Similarly, the impact of TiO_2 and CeO_2 NPs on microbial action during AD was studied by Garcia et al. [49]. In this case, 640 mg/L CeO_2 hindered the generation of biogas up to 100%, but TiO_2 NPs exhibited no or minimal inhibition under mesophilic temperatures. In thermophilic temperatures, TiO_2 NPs addition in AD had a satisfactory effect which promotes 10% increase in biogas generation. However, CeO_2 NPs strongly inhibited the microbial activity in thermophilic circumstances with a 90% inhibition rate. Additionally, Zheng et al. [47] found that even at high concentrations of 150 mg/g TSS TiO_2, NPs had no effect on sludge hydrolysis and acidification in both short- and long-term exposure, which did not result in the enhancement of methane generation during AD.

Using TiO_2 to pretreat the waste-activated sludge enhanced methane production at the dosage of 0.03 g/g SS. An increase in biogas generation was found in on-site TiO_2 pre-treatment of waste-activated sludge. The methane production increased up to 1266.7 mL/L of sludge and volatile elimination up to 67.4% was achieved in the anaerobic digestion process [50]. To investigate the effect of metal oxide nanoparticles on biogas production, two dosages of TiO_2 (100 and 500 mg/L) were added to substrate along with the iron oxide (Fe_2O_3) for AD. Higher methane and biogas production was observed at 500 mg/L TiO_2, which produced 1.17- and 1.21-times increased biogas and methane generation compared to the control sample. The experts revealed that the substrate treated with single metal oxide NPs generated a higher quantity of methane than the substrate with mixed NPs. These results are consistent with the findings of Garcia et al. [50], which observed 10.0 and 14.9% of excess biogas generation, respectively, when compared to control samples. The findings strongly suggest that employing metal-oxide NPs boosts the AD process, which is a viable option.

2.3. Carbon-Based Nanomaterial

The usage of carbon-based nanomaterials in AD systems has inspired a great deal of attention due to its effective physical and chemical potentials (such as high electrical conductivity and adsorption). Some of the highly utilized carbon-based nanomaterials for waste management are graphene, activated carbon, biochar, carbon nanotubes, carbon felt, and carbon cloth in AD systems. This nanomaterial favors the growth and development of microorganisms by providing genial adaptable environmental conditions [51]. The function of various carbon-based nanomaterials was provided in Figure 5.

These carbon-based nanomaterials offer an excellent immobilization matrix for microorganisms, which increases activities of microbes, electron transfer between anaerobes, and biogas generation, which was detailed in Table 3.

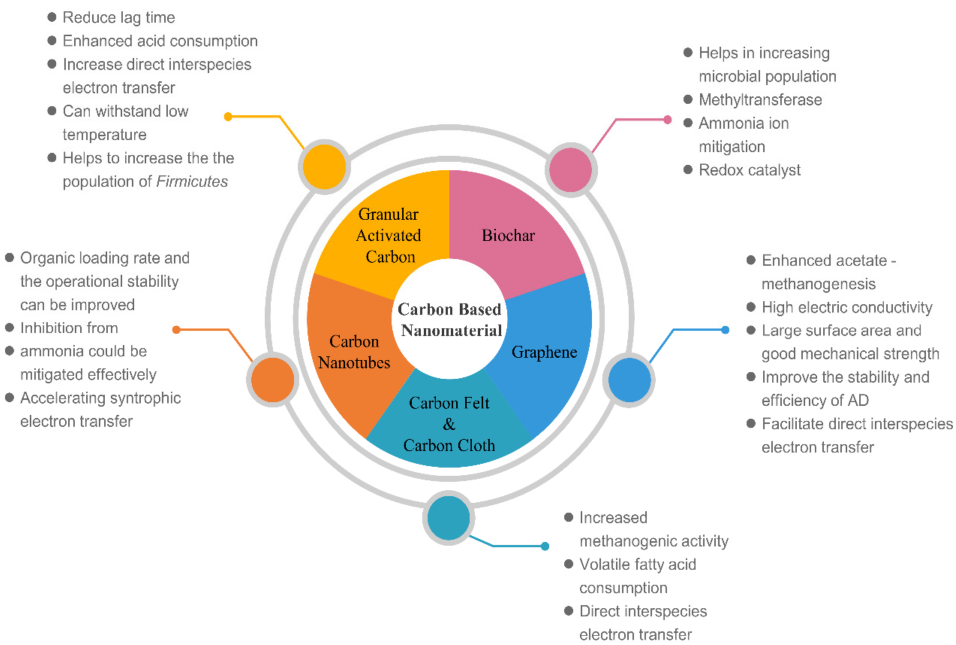

Figure 5. The function of various carbon-based nanomaterial in enhancing AD.

Table 3. Various carbon-based nanomaterial involved in AD enhancement.

S.No	Substrate	Cabon-Based Nanomaterial	Dosage	Methane Generation	Scale of Work	Inhibition/ Stimulation	References
1.	Waste-activated sludge	Graphene oxide	0.108 mg/mg VS	−12.6%	Lab scale 10 L	Inhibition	[52]
2.	Waste-activated sludge	Graphene oxide	0–300 mg/L	NA	Lab scale 10 L	Inhibition	[53]
3.	Sludge	Graphene	30 mg/L (5 mg/g)	14.3%	Lab scale 500 mL	Stimulation	[54]
			120 mg/L (20 mg/g)	51.4%		Stimulation	
4.	Sludge	Carbon fibers	Specific surface area = 1.6 m^2/L	50%	Lab scale 200 mL	Stimulation	[55]
		Biochar	2.5 g/L		Lab scale 200 mL		
		Graphite	Surface area 200 cm^2/L		Lab scale 200 mL		
5.	Dewatered activated sludge and food waste	Biochar	15 g/L	NA	Lab scale 1 L	No stimulation	[56]
6.	Activated sludge	GAC	5 g/L	17.1%	Lab scale 150 mL	Stimulation	[57]
7.	Seed sludge and waste water	GAC-Fe_3O_4	40 g/L/25 g/L	34%	Lab scale 500 mL	Stimulation	[58]
8.	Seed sludge	GAC-Fe_3O_4	13.5 g/L	20%	Pilot Scale 500 mL	Stimulation	[59]
9.	Food waste sludge	AC	15 g/L	41%	Lab scale 250 mL	Stimulation	[60]
10.	Sucrose/sludge	Single-walled carbon nanotubes (SWCNT)	1 g/L	NA	Lab scale 500 mL	No stimulation	[61]

Graphene is a stratified nanostructure with strong conductivity and strength, which help with methane production. Graphene was added to sludge as a feedstock during AD, which increased methane output by 25%. The effect of graphene on AD was explored at different doses of 30 mg/L and 120 mg/L, resulting in 15% and 51% increases in methane output, respectively [54]. However, the graphene dioxide showed inhibition during the AD process. The incorporation of graphene into AD enhances the syntrophic relationships with acidogenic microorganisms and methanogenic archaea, along with increasing CH_4 synthesis by 28% through Methanosarcina and Methanobacterium via direct interspecies electron transfer (DIET).

Activated carbon assists in the adsorption of gaseous pollutants which have a large surface area and a porous structure. As a result, activated carbon is commonly utilized to avoid the inhibitory phases induced by excess ammonia concentrations, which are mainly focused to minimize odor emissions during AD, which has the advantage of CH_4 generation and reduction of air pollution. Because of the influence of DIET on AD performance, granulated activated carbon (GAC) enhances the methane generation Zhang et al. [60]. Distinct microorganisms receive electrons from this GAC, which was employed as a support medium to boost biogas generation. GAC-enriched hydrogen-utilizing *methanogens* and *Geobactor* stimulates DIET, which increases the exchange of electron between syntrophs and methanogens. Moreover, utilizing GAC for waste-activated sludge (WAS) digestion resulted in a 17.4% increase in methane output for dosage ranges from 0.5 to 5 g/L. GAC existence boosted the electron transport between methanogen and fermenting bacteria. Specific methanogens enriched by activated carbon increased CH_4 generation by 72%. On observing AD of synthetic brewery wastewater with GAC and powdered activated carbon, both carbon-based nanomaterials had exactly the same effect.

A combustible solid generated during the pyrolysis of biomass is Biochar, which is a kind of activated carbon with a porous and conductive structure that can minimize the inhibition of ammonia and immobilize methanogens through adsorption, making it a potential material for improving the AD process efficacy [61]. Biochar has useful features, such as porosity, high conductivity, and surface area, which are attributed to its beneficial physicochemical properties [62]. These characteristics aid in the modification of microbial populations in symbiotic connections. Furthermore, by immobilizing degrading bacteria and enriching cell concentration, biochar with strong electrical conductivity might promote organic matter decomposition. At a concentration of 10 g/L, a 21% improvement in methane production has been documented [63]. When compared to fine biochar, porous biochar promotes biofilm formation, while coarse biochar with a smaller specific surface area improves methane generation. The use of biochar during waste-activated sludge digestion resulted in a 30–45% increase in methane production [64]. Although the electrical conductivity of biochar is far lower than that of GAC, the methane production enhancement is almost effective. Accelerating and equilibrating hydrolysis, methanogenesis, acidogenesis, acetogenesis, and reducing inhibitory stress are all significant actions of biochar. Biochar can help with CH_4 generation by acting as a support. Meanwhile, creating an effective microbial community methanogen-to-methanogen and electron-transfer chain enhances the microorganisms that digest the organic component. The effect of stimulation on CH_4 generation relies on the capacity of charcoal to donate electrons. Biochar was added to the mix, which resulted in better biodegradation. COD of the digestate increases as a result of the use of organic substrates during the sludge AD [65]. Biochar powders have been developed to double the number of cells in the thermophilic AD resulting in a 13% rise in CH_4 output.

By establishing a healthy habitat for the bacterial populations, the inclusion of multi-walled carbon nanotubes (500 mg/kg) successfully boosted 33.6% of CH_4 output (Chen et al., 2020). Furthermore, due to improved DIET kinetics, the multi-walled carbon nanotubes of 5 g/L boosted CH_4 production by 50% [66]. For the purpose of increasing CH_4 generation, single-walled carbon nanotubes (1000 mg/L) were introduced to an AD system. Li et al. [67] found a two-fold increase in methane generation during sludge digestion in which single-wall carbon nanotubes of concentration 1 g/L were added to the seed sludge and sucrose as substrate. It was also found that sludge handled using GAC and single-wall carbon nanotubes (1000 ppm) using glucose as a substrate produced equivalent amounts of methane. Zhang et al. [67] achieved an increase in methanogenic activity when treated with multi-wall carbon nanotubes of concentration 5 g/L and resulted in 50% increment in methane production. After 96 h of AD, multi-wall carbon nanotubes of concentration 1500 mg/L were added to the seed sludge, which increased the cumulative methane production by 43% compared to a control sample. The microbial population altered dramatically at the phylum level due to subsequent long-term exposure to multiwalled carbon nanotubes, with dominant microbes *Saccharibacteria*, *Proteobacteria*, *Chloroflexi*, and *Thermotogae*. Furthermore, proliferation in *Methanoculleus* was observed, signifying that the existence of multiwalled carbon nanotubes aided in the development of these methanogens.

Carbon cloth is a woven fabric made up of conductive fibers that have been shown to aid in the promotion of DIET. When compared to a control sample, using carbon cloth in the anaerobic digestion process increased methane production by 1.3 times. Carbon cloth and carbon felt employed in the AD process improved CH_4 output by 30 to 45%. In methanogenic bioreactors, carbon cloth and carbon felt are used to increase CH_4. By enriching the *Methanosarchina* and *Sporanaerobacter* on the carbon surface, carbon cloth and carbon felt also augmented CH_4 output [68]. Significantly, the addition of carbon fabric, Geobacter strains lack pili and c-type cytochromes that potentially increase the mutual transfer of electrons with Methanosarcina barkeri [69]. On the highly conductive cloth surface, Sporanaerobacter and Enterococcus species were abundant, which proved to transmit electrons to Methanosarcina species and metabolize fermentable substrates. Although carbon nanoparticles can significantly boost biogas generation, their expensive cost prevents it from becoming widely used. The cost of carbon-based nanomaterials must be reduced for future AD research to progress.

2.4. Nanocomposite Material

The comparatively dense micronutrients that appear as NPs may promote quasi distribution and aggregation of NPs in the AD medium, lowering resource accessibility and diminishing the physicochemical association between NPs and microbes. Encapsulating or binding numerous chemicals in combined NPs to form nanocomposite material has distinct properties. The major advantage of supporting/coating the NPs onto carrier additives is to: (1) rectify the cytotoxic activities of NP aggregation and (2) strengthen the bonding of microbes and NPs improving NP reactivity and performance. Metal/metal oxide NPs (i.e., TiO_2, Al_2O_3, SiO_2, zeolite, carbon-based materials, etc.) distributed across support materials to enhance the proportion of NPs with surface-exposed atoms which boost reactivity owing to their intended dispersion over the support surface. Hassaneen et al. [70] designed and synthesized zinc ferrite (ZnFe), ZnFe with 10% carbon nanotubes (ZFCNTs) and zinc ferrite with 10% C76 fullerene (ZFC76) as nanocomposite material to enhance methane production from organic waste. The maximum methane enhancement was observed in ZnFe, which endorsed methane generation to 185.3%. ZFCNTs and ZFC76 had a beneficial impact on the hydraulic retention time (HRT) and improved the generation of methane to 162% and 145.9%, respectively, compared to the blank reactors. Amen et al. [35] investigated the effects of several additives on the AD of household sludge in mesophilic conditions, including zeolite, NZVI, NZVI-coated zeolite (ICZ) particles, and NZVI and zeolite mixture. The addition of ICZ caused a lag phase before considerable biogas volume was generated as a result of ammonia buildup at the start of the digestion period, according to experimental monitoring. Because large levels of ammonia (>400 mg/L) hinder particular enzyme processes, this is the case. However, following the lag period, the cumulative production of ICZ was higher than that of the other additives studied, namely NZVI, zeolite, NZVI, and zeolite combination. Furthermore, larger Fe NP concentrations on the surface of zeolite particles resulted in increased biogas production. The high rate of biogas generation is most likely attributable to the effect of ICZ particles (1000 mg/L), which improve bioavailability thoroughly for non-uniform dispersion in the digester medium and the interaction between the exogenous additives in terms of electron transfer as well as the microbiome.

Additionally, carbon nitride/titania nanotubes (C_3N_4/TiO_2 NTs) composites were synthesized for the enhanced visible-light-mediated photocatalytic degradation and pretreatment of wastewater sludge for enhanced biogas production [71]. Chitosan/TiO_2 nanocomposite film can be used as an EPS extraction technique and pretreatment of dairy sludge to enhance the methane generation to 140.40 mL/g COD (during EPS removal) and 235.6 mL/g VS (during pretreatment) [72]. Zhang et al. [73] explored the effects of supported nanoscale zerovalent iron (nZVI-BC) for methane production and its effects on the microbial structure at mesophilic temperature. This biochar-supported nanoscale zerovalent iron (nZVI-BC) was produced and employed as an additive during AD of sewage sludge. The addition of nZVI-BC improved process stability by enhancing the synthesis and degradation of intermediate organic acids, while excessive dosages resulted in inhibitory effects. The total methane yields and methane content were both raised by 29.56% and 115.39%, respectively.

3. Environmental and Economic Impact

Commercial utilization of the nanomaterial poses certain limitations and risks in environmental and economic aspects during large-scale implementation. It is significant to evaluate the environmental risk of nanomaterial usage in biogas production prior to discharge of the effluent after AD. Reduction and recovery is the key solution to minimizing the environmental risk associated with nanoparticle usage. Certain measures can be preferred to prevent or reduce the environmental threats of using NPs. Most of the nanoparticle has recycling potency to decrease the discharge of NPs as such into the environment with effluent from the industries [74]. Hence, instead of using fresh NPs for the AD process, waste containing NPs which were already disposed into the environment can be recovered and reused. The digestate remained off for disposal containing certain remediating NPs such as Zn and Cu that could be remediated, i.e., Zn to ZnS, and can be reutilized as agricultural fertilizers. In addition to this, production of NPs using natural resources prevent the risk associated with effluent disposal [75].

Another method is to recover NPs prior to disposal. Instead of disposing of the NP with digestate, several studies outline the way to recover the NPs inside the AD reactor itself. Hussein et al. [76] followed three sets of recovery strategies:

i. The liquid samples were collected, dried, and coated on a carbon substrate at 35 °C.
ii. Both the liquid and solid samples were collected, dried, and coated.
iii. Both the solid and liquid samples are collected within the reactor using a magnetic stir bar enclosed with plastic parafilm.

Among the three, the third option is considered effective for recovery of the NPs of metallic constituents, but it cannot recover non- metallic NPs. Hence, the first and second method can be chosen for such cases. In addition to this, another method of recovering the NPs is immobilization of NPs inside the bed of the reactor through various immobilization techniques such as the sol–gel method, sputtering method, etc. [77–79], and usage of nanocomposite film, which was also attempted by various researchers. Hence, more attention and research on this aspect to prevent environmental risk is mandatory.

The economic feasibility of using nanomaterial for biogas production mainly relies on the amount of biogas energy produced and revenue generated along with the cost of NPs utilized in the digestion process [80]. Energy and cost-benefit analysis was performed by Abdelwahab et al. [18] to study the effect of usage of various NPs (Ni, Fe and Fe_3O_4) in AD. It was found that among the three NPs, Fe showed higher energy content of 403 kWh with a net profit of USD −676.5, whereas low net-energy (192.6 kWh) and net profit (7.2 USD) were achieved during the usage of 5 mg/L of Fe NP. Additionally, Ni NPs achieved a good net profit of USD 20.6 with 231 kWh energy at the dosage of 1 mg/L. Utilizing 23.5 mg/L of NiO-TiO_2 NPs produced 75.84 kWh of biogas. In this study, the cost of energy consumption was considered 0.0612 Euro/kWh based on the price status of Denmark. Additionally, consumable cost for TiO_2 NPs is estimated as 2000 EUR/Ton. The net profit achieved was EUR 0.29, which was 7% higher than the control sample. Liu et al. [28] studied the usage of nZVI and Fe_3O_4 NP usage in AD. The economic evaluation confirmed that using iron NPs could save 272,400 USD/year and cut down carbon emissions by 1660 tCO_2/year compared to the traditional AD process.

4. Future Perspective on AD Enhancement

Despite the fact that AD research was developed long ago, the restriction in industrialization was due to the various issues in AD efficiency. Further investigation has been carried out to improve the efficiency of the AD by optimizing the parameters for enhancing microbial existence during the digestion process and improving the hydrolysis process [26,81]. Nanomaterials in this regard would be a candidate to replace many other conventional materials/processes for more efficient sludge biodegradability [31,82]. The usage of various NPs in AD is the growing trend for sustainable and feasible application of methane production [32,83]. One of the major challenging facts is the implementation of the process on an industrial scale since the degradation time, the catalytic role of NPs, and microbial interaction with the NPs require more investigation. Combating the substrate inhibition, buffering stabilization, and microbial colonization area are highly focused during AD enhancement. Further research regarding the interaction between NPs and microbes, buffering capacity, and impact of biomass content is required. Usage of NPs in suspension is not highly recommended for the industrial sector, since the fate of NPs in the digestate may induce a harmful impact on the environment which requires more investigation [15,81]. Hence, proper research is still necessary to estimate the syntrophic conversion of the various substrate with NPs for various kinds of anaerobic digesters. A more thorough investigation is also important to validate the metal fractions and bioavailability in anaerobic circumstances [82,83]. Furthermore, additional exploration of the synergistic effects of multi-nanoparticles on metal specifications, particularly the production of metal sulfides in sulfite-rich environments, is required. Impacts related to changes in particle properties of nano-additives with the same chemical components, including the depression degree and stability of the nanoparticles in the liquid phase, are still unclear in the literature. As a result, a series of studies should be performed to find an optimal size range, optative morphologies, and the best dispersion solution, as well as appropriate pretreatment for each metallic nano-additive.

5. Conclusions

Addition of various nanomaterials on WAS has both a positive and a negative impact on the AD process. However, utilizing NPs in powder form on a larger scale is not encouraged due to issues of both economic feasibility and NP outcome in effluent, which may have a negative impact on the environment. Possible approaches for commercializing Nanoparticles use in AD systems include depositing NPs on the surface of the substrates such as glass, polymers, etc., to prevent the release of NPs into the environment. It was observed that most NPs play a significant role in enhancing the biogas production capacity. Addition of metal oxide NPs showed mixed effects on biogas production, as it depends on the concentration, types, and size of NPs as well as the substrate type. The addition of zero-valent NPs showed a positive effect on biogas production. The addition of carbon-based NPs shows a positive effect on the concentration of ammonia, consumption of VFAs, and COD. Using an NPs mixture reduced H_2S production by 100% depending on the NPs mixture concentration. Usage of the waste containing NPs generated by other industries, natural NPs, and improving the methods to recover the NPs inside AD reactors could decrease the environmental risk of NPs. Only a few pieces of information regarding the parameter, methanogenic activity inhibition, and toxicity effect were identified. Therefore, further investigation is still needed to provide a deep analysis of the AD process and biogas production. This proposed review summarizes the involvement of various NPs in the digestion method to the point of identifying the knowledge gaps and proposing future research pathways to specify the obvious structure of the research path for enriching the sludge digestion efficiency.

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