Nanoparticles for Biogas Producers

Subjects: Nanoscience & Nanotechnology

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Nanotechnology has an increasingly large impact on a broad scope of biotechnological, pharmacological and pure technological applications. The novel notion of dosing ions using modified nanoparticles can be used to progress up biogas production in oxygen free digestion processes.

biofuels bio-methane environment nanoparticles nanotechnology biosensors waste activated sludge

1. Introduction

Over the past few decades, industrialization and population growth has led to a significant increase in energy demand. Currently, fossil fuels are the prime source of basic energy production, contributing 80% of total global consumption. Out of this 80% of primary energy produced by fossil fuels, the transport sector is the major consumer with 58% consumption [1][2], of which 80% is being produced by Brazil and USA [3]. In future, the transportation fuel demand is estimated to increase up to 55% globally by 2030 and this will increase the demand for biofuels [3][4][5].

Due to this intensive consumption and increasing demand in the energy sector, fossil fuel resources are depleting at a rapid pace and there is a dire need to explore and identify new and renewable energy sources globally [6].

One such renewable energy source is biogas produced by anaerobic digestion (AD), which utilizes various wastes such as animal manure, [7] agricultural waste [8] and organic wastes [9]. Biogas is produced mainly due to the process of AD, resulting in the formation of CO_2 as a byproduct, which is consumed during photosynthesis and retrieved again, for AD, in the form of agricultural waste and animal manures. This consumption of CO_2 takes place in a closed cycle [10], as shown in Figure 1.

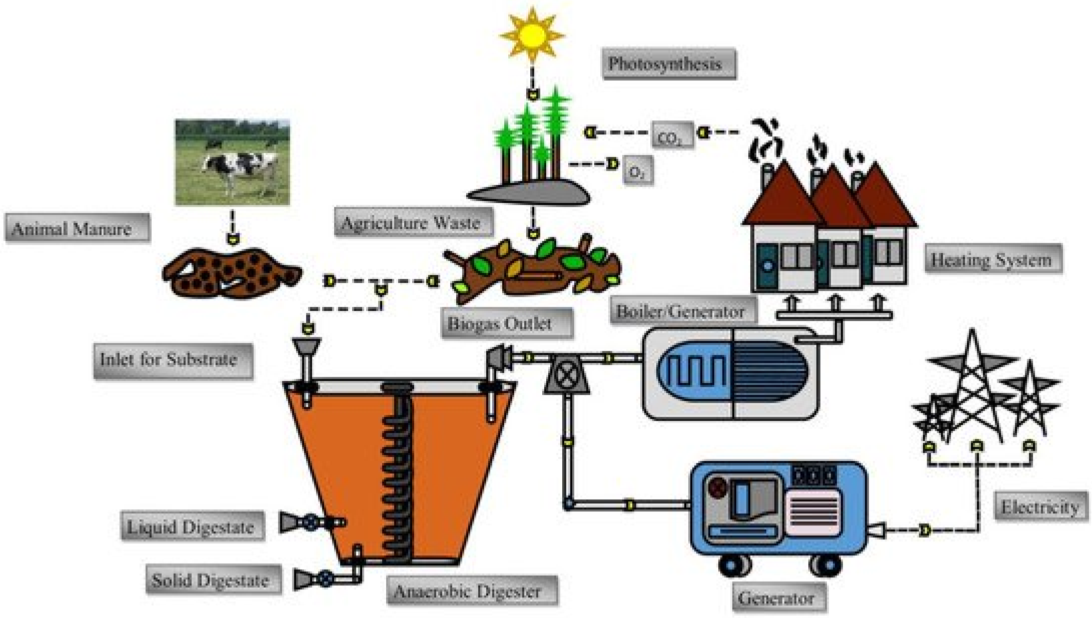

Figure 1. Waste utilization to produce renewable energy.

During AD, four steps are involved in methane production, which include; hydrolysis, acidogenesis, acetogenesis, and methanogenesis. Methane production is a result of the synthrophic microbial relationship. During hydrolyses, bacterial cellulosome and exoenzymes monomerize complex proteins, carbohydrates and fats. In the second step (acidogenesis), along with CO_2, hydrogen and alcohols, further degradation of monomers into short chain acids takes place. In the third step (acetogenesis), short chain acids are converted into acetate, CO_2 and hydrogen. In the last step (methanogenesis), intermediates are converted into CO_2 and methane by methanogens [11] (Figure 2).

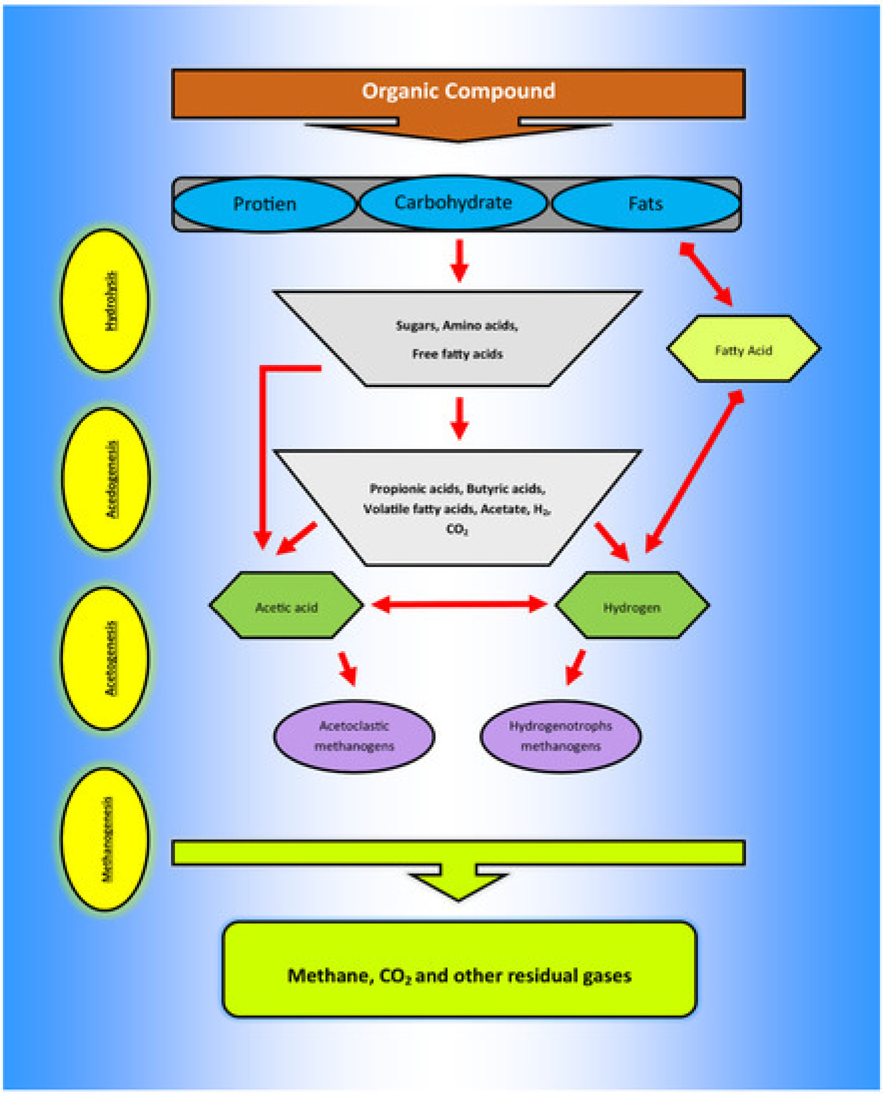

Figure 2. CO_2 and biomethane formation in an anaerobic process.

2. Application of Biosensors in Biogas Monitoring

The assessment of anaerobic digestion is based on the continuous monitoring of organic and volatile fatty acids, resulting in the accumulation of intermediates for unsteady progression conditions [12]. The intensifying public interest in biogas production is a result of the exhaustion of fossil fuels. Anaerobic digestion has the advantage of exploiting industrial waste for energy production and thus treating another modern day problem [13][14]. Efficient methane production and endurance of process stability are resulting outcomes based upon the improvement of several economic and technological aspects. These include a suitable feedstock composition, appropriate biogas purification technologies and ideal conditions for a biogas reactor, which is based upon several physical and biochemical parameters, including pH, alkalinity, gas quality, FOS/TAC (Flüchtige Organische Säuren, i.e., volatile organic acids/Totales Anorganisches Carbonat, i.e., total inorganic carbonate) [15][16][17]. The accumulation of organic acids like formate, lactate and alcohols, and volatile fatty acids (e.g., propionate, acetate, butyrate) results in acidification of the reactor, which clearly indicates process imbalance [18][19][20][21]. The conventional methods for estimation of acid composition are gas chromatography [22], spectroscopy [23][24] and HPLC (high-performance liquid chromatography) [25][26], which are commonly carried through external sources that cause high cost partanalysis.

3. Metallic Nanoparticles Used for the Enhancement of Bio Gas Production

3.1. Nanoparticles

‘Nanomaterials’ are the materials with an external dimension or internal or surface structure on a nano scale ranging from 1 to 100 nm in size [27][28]. The chemical origin of nanoparticles is greatly influenced by their chemical origin, which is responsible for their behavior and fate in the environment [29][30]. Nanoparticles are classified into four groups: organic, inorganic, composite and carbon NPs. Nanoparticles possess special chemical, physical and optical characteristics. At the nano scale, properties of the particles change unpredictably, making them behave differently with the same substance at the macro scale. Nanoparticles are ideal in a diversity of areas, such as energy, medical, electronic and commercial products, due to their high reactivity and special features. Using nanoparticles leads to the production of efficient, durable, lighter, firmer, and cleaner products and materials [31].

Different chemical and physical properties of nanoparticles from their macro counterparts make them interesting. The higher chemical reactivity of nanoparticles is due to their high surface area, providing a greater number of reaction sites [32]. Gold (Au) is another example of nanoparticles at the nano scale. Amber does not react with many chemicals at the macro scale and behaves as an inert element, but at the nano scale, gold becomes enormously reactive, behaving as a catalyst to speed up reactions [32]. This extremely reactive property of nanoparticles is due to the ratio between the mass and open area. The human digestive system is a biological example of AD processes being determined by the surface area to volume ratio, microorganism activity aids AD digestion.

3.2. Concentration of Nanoparticles

Nanoparticles have been acquired from both anthropogenic and natural resources. In waste sludge, a very high concentration of NPs could have accumulated. However, the toxicity and the impact of NPs on the sludge treatment stream is still an area that requires a great deal of research [33]. Nguyen determined the effects of ZnO NPs and CeO_2 nanoparticles on the sludge AD process, toxic potential of sludge to plants and bacteria and dewatering process of the sludge.

The concentration of nanoparticles is very important in determining their role for the process of methane and biogas production (Table 1). Not all nanoparticles stimulate the anaerobic digestion system, rather some nanoparticles inhibit the production rate considerably when compared with a controlled sample. Types and concentration of nanoparticles play a vital role in the production rate of the anaerobic digestion system. In comparison with a control sample, the exposure concentration of ZnO at 1000 mg/L resulted in inhibition to 65.3%

biogas volume and 47.7% methane composition. At an endurable exposure concentration of zinc oxide, the inhibition effect could be overcome after an incubation of 14 days [34].

Table 1. Nano additives concentration and their impact on the biogas and methane production rate.

NPs Type	NP size	Concentration	Feedstock	Temperature	Incubation Time	Effect
CeO_2	192 nm	10 mg/L	Sludge from UASB reactor	30 °C	40	11% Increase in biogas production [33]
Fe_3O_4	7 nm	100 ppm	Waste water Sludge	37 °C	60	180% Increase in biogas production and 234% increase in methane [35]
Fe/SiO_2		105 mol/L	–	55 °C	–	7% Increase in methane production [36]
Pt/SiO_2	–	105 mol/L	–	55 °C	–	7% Increase in methane production [36]
Co/SiO_2	–	105 mol/L	–	55 °C	–	48% Increase in methane production [36]
Ni/SiO_2	–	105 mol/L	–	55 °C	–	70% Increase in methane production [36]
Co	28 nm	1 mg/L	fresh raw manure	37 °C	40	71% increase in biogas production
						45.92% increase in methane production [37]

NPs Type	NP size	Concentration	Feedstock	Temperature	Incubation Time	Effect
Ni	17 nm	2 mg/L	fresh raw manure	37 °C	40	78.53% increase in biogas production 116.76% increase in methane production [37]
Fe	9 nm	20 mg/L	fresh raw manure	37 °C	40	47.7% increase in biogas production 67% increase in methane production [37]
Fe_3O_4	7 nm	20 mg/L	fresh raw manure	37 °C	40	73% increase in biogas production 115.66% increase in methane production [37]
ZnO	140 nm	1 mg/g-TSS 10 mg/g-TSS 50 mg/g-TSS	WAS AGS	35 °C	40 105	No effect [38] No effect [39] No effect [39]
nZVI	<50 nm	10 mg/g-TSS	WAS	37 °C	30	120% increase in methane production [40]
Fe_2O_3	<30	100 mg/g-	WAS	37 °C	30	117% increase in methane

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NPs Type	NP size	Concentration	Feedstock	Temperature	Incubation Time	Effect
	nm	TSS				production [40]

4. An Understanding of Biomass and Their Characteristics

Biomass resources were analyzed on the basis of chemical, biological, physical composition and in terms of their source. Evaluation of the impact of biomass particle size on the biomass to bioenergy conversion basis was carried out, in both biothermal and biochemical aspects. Different biomass types were studied based on pretreatment and particle size. In terms of structure and composition, different effects were produced by different pretreatment methods [41]. For example, lignin can be removed from alkaline pretreatments, and the biomass hemicellulose fraction can be removed by acidic and biothermal pretreatment. Reduction in particle size to increase the biomass specific surface can be carried out to reduce cellulose fiber organization during biomass fibrillation by a milling-based pretreatment, measured by a decline in crystallinity.

Enhancement of economically leveraged renewable energy production and energy efficiency can be done with the help of nanotechnology. Nanomaterial interactions were evident with a few algal biomass species and active sludge. With regards to bioenergy production inhibitory [33], an adverse or increased yield [42] was visible. Particle surface area to volume ratio, leading to variation in the severity of the effects, was also assessed. NPs' effects on energized sludge systems. The outcomes of the NPs impact on energized sludge can be seen in a few related characteristics of NPs and energized sludge. These include aggregation, size of nanoparticles and reciprocation of microorganisms in its bioenergy production.

5. Nanoparticles with Microorganisms

Nanoparticles have significant effects on microorganisms. NPs strain latent detrimental effects on wastewater microorganisms, according to an overview of their antimicrobial properties. Although, at present, statistical data on the NPs' effect on wastewater microorganisms during aerobic digestion are rather minimal, but it still has a remarkable effect [43][44]. Hence, it is tough to make a particular claim regarding the harmful effect of NPs on wastewater microorganisms. However, minimized efficiency of AS and AD processes, absolute collapse of treatment and environmental pollution from contaminated effluents and utilization of biosolids for changes in soil texture may result due to NPs and microbial community contact [45].

A broad range of microorganisms are affected by the silver ion. Bacterial growth in a variety of medical treatments, including dental work, catheters, and healing burn wounds, has been controlled in recent days by silver ions [46]. Concentration and contact time influencing the mechanism of release of ions from Ag was exhibited by *Escherichia*

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coli. The leaking of reducing sugar and protein, enzyme inhibition and obstruction of the dispersed vesicles, which slowly disintegrate, are the detrimental effects inhibiting cellular respiration and cell growth [47].

6. Modified NPs, Particle Size and Their Effect

Excessive use of nanotechnology resulted in large-scale manufacturing and utilization of engineered nanoparticles (ENPs) on an industrial level. In comparison with CNTs and Ag nanoparticles, natural nanoparticles exist in a massive amount in the environment. Since natural NPs are generated in an uncontrollable way, most of the research has related to characterization and focused on ENPs. A mixture of ENPs containing ZnO (20 nm), AgO (20 nm) and TiO_2 (30–40 nm) were compared with their bulk metal salts to evaluate their effects against non-spiked activated sludge (control) [48]. This study was conducted using three pilot treatment plants on a pilot scale. In comparison with the control plant, the specific oxygen uptake rate (SOUR), specific to microbes, increased 200% by introducing both nanoparticles and bulk metal mixtures. Selective damage was shown by scanning electron microscopy (SEM) on some microbial cells. Furthermore, due to the presence of NPs, floc size of activated sludge also reduced, but sludge volume index (SVI) remained the same. Various environmental factors such as sludge volume index (SVI), natural organic matter, pH, light, etc., can affect the behavior and fate of NPs in the environment [49]. Bioavailable, chemical and physical properties of releasing NPs can be affected by various influences in nature.

It is very important to assess the potential risk of nanomaterials and nanoparticles by organizing the expected transformation and stability, and their interaction with other materials [29]. The behavior and toxicity of the impact of NPs on terrestrial and aquatic media is determined by the shape and particle size [50]. For example, nanoparticles with a size less than 30 nm produced a more cytotoxic effect to *S. aureus* and *Escherichia coli* [51] than an 8090 nm particle size [52]. This study proves that an AgO particle size greater 30 nm is unable to inhibit the microbial process. Size less than 5 nm in suspension is of particular interest due to its capability of nitrification inhibition in AS [53]. As shown for AgO, along with particle size, shape also plays a vital role and they can exist in rod, triangle or spherical shape. Out of these three distinct particle sizes, the truncated triangle form of silver oxide produced the strongest antibacterial effect on *Escherichia coli* in both broth and agar cultures [54]. There is no evident conclusion of this observation from pure culture to complex wastewater because microbial cells' interaction with NPs can be attenuated or enhanced by wastewater components.

7. Phytotoxicity/Ecotoxicity Effect of NPs

The effect of nanoparticles on inhibition in relation to the performance of AD needs to be investigated. Moreover, the sludge after digestion through AD is applied as compost and soil conditioner by dewatering. However, this sludge becomes inappropriate and toxic to apply as a biosolid due to the accumulation of nanoparticles. Therefore, digested sludge containing nanoparticles should be assessed in relation to phytotoxicity, and bacterial toxicity should be assessed before reusability of waste sludge. Moreover, further studies are required to find out the effect of nanoparticles on the dewatering ability of digested sludge. Therefore, it is not obvious whether nanoparticles can

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hinder the dewatering ability of digested sludge. Elimination of nanoparticle toxicity during AD, or can cause inhibition effects on plants and bacteria. These questions still need to be answered [55].

There has been a significant focus on aquatic, rather than terrestrial, plants in term of ecotoxicity. Toxic effects of nanoparticles, on the germination and root growth of some plant species, have been reported in some studies [56]. One of these studies was designed to compare the effects of five types of commonly used nanoparticles with their corresponding bulk material in regards to biomass, germination and root elongation in the Cucurbita pepo (zucchini) plant. These particles included multi-walled carbon nanoparticles (MWCNTs), ZnO, Si, Ag and Cu. To ensure the validity of relevant phytotoxic responses, 1000 mg/L was selected. A dose response study determined the effect of nanoparticles or bulk Ag concentration on transpiration, Ag content and biomass of the zucchini plant. Assessment related to the impacts of nanoparticles on agricultural plants will help find out the potential hazards of food chain contamination for human exposure as well as ecological exposure risk related to nanoparticles [57].

8. Mechanism of Microbial Activity

Nanoparticles are toxic to human and other living organisms. Due to their nano scale, they are easily exposed to humans and other organisms through ingestion, inhalation and dermal contacts. A large number of publications by various authors is available on the behavior, characterization and toxicological information of nanomaterials [58]. The focus of this research is mainly on manufacturing of commercialized nanomaterials, which are widely applicable, such as fullerene, metal oxides and CNTs. It is important to assess the fate of nanoparticals on the environment when applying them commercially on a larger scale. Ag nanoparticles are capable of interacting with the surface of various bacterial cells. This is especially relevant when dealing with Gram-negative bacteria because accumulation and adhesion of Ag NPs to the surface of bacteria has been observed in numerous studies. By damaging cell membranes, Ag NPs lead to structural changes, making bacteria more permeable [59]. This change is directly related to concentration, shape and size of the nanoparticles [60]. This influence is confirmed by a study using *Escherichia coli* that affirmed that gaps in the integrity of the player are created by the accumulation of Ag NPs, which increased the permeability leading to cell death of bacteria [61].

Due to their widespread medical, military and industrial applications, metal oxide nanoparticles, such as zinc oxide (ZnO), silicon dioxide (SiO_2), aluminum oxide (Al_2O_3) and titanium dioxide (TiO_2), have gained a lot of interest. They affect soil, aquatic organisms and human health upon their release into the environment. So far, the mechanism of toxicity for each nanoparticle is not understood exactly, but various characteristics may result in damage to the exposed organisms. Reactive oxygen species (ROS), such as super oxides (O_2^-), singlet oxygen ($^1O_2$) and free radicals (OH^-), are generated by nanoparticles that employ various adverse effects on microbes, such as scattered vesicles, disruption of cell wall, enzyme inhibition and protein and sugar membrane leakage leading to slow dissolution and resulting in inhibition of cellular growth and respiration [47][50]. During some studies, the metal oxide nanoparticles, ZnO, SiO_2 and Al_2O_3, were proven harmful to *Pseudomonas fluorescens*, *Bacillus subtilis* and *Escherichia coli* [62]. Significant toxicity was caused by these nanoparticles to the viability of Gram negative bacterial cells by increasing their antibacterial effects. Chen et al. [63] reviewed the toxicity of nanomaterials on biomass and found that the chemical stability of nanoparticles of Ag, TiO_2, Al_2O_3 and SiO_2 have

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