

Utilization of nanoparticles for sustainable biogas production: process stability and effluent quality

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Systematic Review

Keywords: Anaerobic digestion, Metallic nanoparticles, Metal oxides nanomaterial, Cattle manure treatment, Effluent

Posted Date: April 18th, 2022

DOI: <https://doi.org/10.21203/rs.3.rs-1554320/v1>

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Abstract

One of the most important techniques for converting complex organic waste into renewable energy in the form of biogas and effluent is anaerobic digestion (AD). Several issues have been raised related to the effectiveness of the AD process in recent years. Hence nanoparticles (NPs) have been used widely in AD process for converting organic wastes into useful biogas and effluent in an effective way. This review addresses the knowledge gaps and summarizes recent researchers' findings concentrating on the stability and effluent quality of the cattle manure AD process using various NPs (e.g., Fe, Ni, Co, and metal oxides). In summary, the utilization of NPs have beneficial effects on methane generation, process optimization, and effluent quality. Their function, as key nutrient providers, aid in the synthesis of key enzymes and co-enzymes, and thus stimulate anaerobic microorganism activities when present at an optimum concentration (e.g., Fe NPs 100 mg/L; Ni NPs 2 mg/L; Co NPs 1 mg/L). Furthermore, utilizing Fe NPs at concentrations higher than 100 mg/L is more effective at reducing hydrogen sulfide production than increasing methane, whereas Ni NPs and Co NPs at concentrations greater than 2 mg/L and 1 mg/L, respectively, reduce methane production. Effluent with Fe and Ni NPs showed stronger fertilizer values more than Co NPs.

1. Introduction

Energy "powers" provides us with pleasant light and temperatures in our living spaces and working environments; it feeds manufacturing plants, urban infrastructure, and the multitude of electronic assistants we use in our daily lives; and it allows us to travel around the world almost indefinitely (Kumar et al. 2020; Zakari et al. 2022). The current global energy issues related to the lack of fossil fuels like crude oil, coal, and natural gas, along with excessive gas emissions from excessive utilization of fossil fuels have great concern worldwide (IEA 2020).

Global energy demand is increasing rapidly, rising from 14.00 BTOE (billion tonnes of oil equivalents) today to more than 18 BTOE by 2030. It's also worth noting that worldwide energy consumption increased by 5.3%, 1.5%, and 1.4%, respectively, for natural gas, oil, and coal (BP energy outlook 2019). By 2050, energy demand could be three times what it was in 2020, according to the International Energy Agency (IEA 2020).

Furthermore, fossil fuel combustion has resulted in air pollution, global warming, and climate change (Rogelj et al. 2018; Roy et al. 2020; Hajilary et al. 2020; Bhattacharya et al. 2020; Zhang et al. 2022). An environmental crisis resulting from rising CO₂ emissions and decreasing fossil fuel availability leaves no other option but to find a new clean and sustainable energy source. There is a shift away from fossil fuels and toward renewable energy sources (Baena-Moreno et al. 2019; Dalmo et al. 2019; Dlamini et al. 2019; Ghosh et al. 2019; Oliveira et al. 2019; Sharma et al. 2019; Vaish et al. 2019).

Renewable energy sources such as biomass, hydro, wind, solar, geothermal, and tide provide about 17.8% of global energy consumption (WBA 2019). In terms of waste management and environmental impact

reduction, biomass and organic wastes are superior renewable energy sources upon fossil fuels (Drożdż et al. 2022).

Animal manure (Chowdhury et al. 2020), agricultural residues (Tamburini et al. 2020), food wastes (Bedoi et al. 2020), sewage sludge (Ghosh et al. 2020), and other energy crops (O'Keeffe and Thrän 2020) are some of the wastes that can be used as feedstock. For animal manure, livestock accounts for roughly 40% of the global value of agricultural products (WHO 2017). Traditional scattered family-scale livestock farms have been steadily converted into centralized ones in recent years to meet an increased demand for dairy and meat products (Li et al. 2020a). These farms produce a lot of manure (cattle, swine, poultry, and sheep) that needs to be treated properly (Li et al. 2020b).

Cattle manure accounts for more than half of all manure produced (Scarlat et al. 2018) and is expected to increase to over 75% in the next decade (Meyer et al. 2018). Cattle manure contains a large amount of undigested lignocellulosic components such as cellulose, hemicellulose, and lignin (more than 50% of total solids) (Abbas et al. 2020; Li et al. 2020b; Tezel et al. 2011; Song et al. 2017; Sahota et al. 2018; Achinas et al. 2017; Zhou et al. 2016; Hu et al. 2018).

Anaerobic digestion (AD) is a complex biochemical process that uses the impact of microbes to convert organic waste into renewable energy in the form of methane (CH_4)-enriched biogas and digestate in the absence of oxygen (Arif et al. 2018; Zhang and Zang 2019; Liew et al. 2022). Biogas is typically composed of 40–75% CH_4 and 25–60% CO_2 , with trace amounts of other impurities such as H_2O (5–10%) and H_2S (1–10000 ppm) (Kadam and Panwar, 2017).

The heat value of biogas with a high CH_4 component is in the range of 20–25 MJ/m^3 . Biogas is a good alternative to fossil fuels since it not only reduces the consumption of conventional energy sources but also reduces green gas emissions by roughly 80% (Arsova 2010). Furthermore, using digestate as a substitute to inorganic mineral fertilizer could minimize fossil fuel usage while also lowering the danger of pollution (Seman et al. 2019; Li et al. 2020c).

To make cattle manure available to anaerobic bacteria, several ways have been used. Co-digestion with other wastes (Jugal and Rao, 2019; Shen et al. 2019; Wei et al. 2019; Akyol 2020; Vijin et al. 2020), pretreatments (chemical, ultrasound, and thermal) (Fernandez et al. 2020; Wahid et al. 2018; Yuan et al. 2019), optimization of operating parameters and bioreactor design (Han et al. 2019; Chen et al. 2020; Farghali et al. 2020). Chemical pretreatment necessitates careful material selection to avoid harmful activities during the procedure (Kaur et al. 2020). Furthermore, ultrasonic and heat treatments can result in significant carbohydrate losses, lowering sugar levels. Physical pretreatment also takes a lot of energy to get the best particle size reduction (Biswal et al. 2020).

Organic additions, such as green biomass and enzymes (Angelidaki et al. 2018; Yuan et al. 2022), and inorganic additives (Romero-Güiza et al. 2016), are utilized to boost CH_4 production in AD processes. Inorganic additives are classified into two types: macronutrients and micronutrients (Dang et al. 2016).

To boost the system buffer capacity and maintain microorganism activity, macronutrients (i.e., P, N, and S) are added to the AD process substrate in the form of salts (Zhang et al. 2018). However, a high dose of bulk materials can cause anaerobic microbe toxicity; also, these materials may not biodegrade efficiently during digestion (Abdelsalam et al. 2017a). Micronutrients (Fe, Ni, and Co) are added to the AD feedstock in the form of salts, bulk materials, and, more recently, nanoparticles (NPs) (Garuti et al. 2018; Wandera et al. 2018).

NPs are particles with three dimensions ranging from 1 to 100 nanometers (Parisi et al. 2015). The chemical composition, dimensions, appearance, condition, and origin of NPs are all used to classify them (Gleiter, 2000; Hochella et al. 2015; Sharma et al. 2015; Wagner et al. 2014). This classification is also based on their size, which in at least one dimension varies from 1-100 nm (Saleh, 2020). In general, NPs have a high surface-to-volume ratio, a large number of particles per unit weight, and confinement or quantum effects, i.e. a small number of atoms per particle. These characteristics of NPs result in properties that are strikingly different from those associated with the same material in its bulk state (Saleh 2020).

In fact, most NPs can absorb inhibiting substances, such as heavy metals, and retain them on their surface (Lei et al. 2018; Zhang et al. 2019). NPs (e.g. Fe, Ni, Co, and metal oxides) stimulate the activation of microorganisms and key enzymes, resulting in more biogas production (Abdelwahab et al. 2020a and 2021c; Abdelsalam et al. 2016, 2017a and b).

Hence, this review aims to provide insights to the influences released by NPs (e.g. Fe, Ni, Co, and metal oxides) on cattle manure AD process in terms of biogas yield (CH_4 , CO_2 , and H_2S), their influences on fundamental mechanisms such as pH, volatile fatty acids (VFAs) and total alkalinity (TA) production, total solids (TS) and volatile solids (VS) degradation, as well as their influences on the characterization of organic materials and chemical composition of the effluent. Finally, perspective on the required future trends and research on the application of NPs in the AD process are highlighted.

2. Iron Nanoparticles

Because of its conductive qualities and inexpensive cost, iron (Fe) NPs have become one of the most popular additions for improving AD performance. Different types of Fe NPs have been shown to stimulate AD (Li et al. 2020a). Zero-valent iron NPs are one of numerous types of Fe NPs that play a role in boosting the AD process. In general, it can act as an electron donor, release Fe^{2+} into the anaerobic system, aid in the production of important enzymes, raise total hydrogen methanogen consumption, shift hydrolysis fermentation types, and increase acetic acid content (Ganzoury and Allam 2015; Suanon et al. 2017; Dehghani et al. 2019; Jadhav et al. 2022).

To begin with, the mechanism of Fe NPs in AD is that when they are oxidized, they release two electrons, Eq. (1). The electron releases provide anaerobic conditions that favour the hydrogenation route. It can also be absorbed by inorganic CO_2 Eq. (2) or acids Eq. (3) to increase CH_4 production. Furthermore,

corrosion can create H₂ from Fe NPs (4). During methanogenesis, H₂ is required for CO₂ conversion (Wu et al. 2020).



2.1 Influences of iron nanoparticles on gas yield

Biogas and CH₄ production are crucial indicators for evaluating AD performance (Amen et al. 2018; Suanon et al. 2017). Using cattle manure at a mesophilic temperature (37 ± 0.5°C), Abdelsalam et al. (2017b) investigated the influence of Fe NPs on biogas production and CH₄ content. They confirmed that Fe NPs have a positive effect on cattle manure at the measured concentrations (5–30 mg Fe NPs/L) by achieving a 44–45% greater biogas yield than the control condition, as well as a 37.6–59.5% higher CH₄ yield than the control experiment (without any additives). According to the author, Fe NP additions could promote CH₄ generation in two ways. To begin with, Fe NPs aided in the production of acetate. Second, Fe NPs act as electron donors in the reduction of CO₂ to CH₄.

Abdelsalam et al. (2016) found that when cattle manure was treated with 20 mg/L Fe NPs and 20 mg/L Fe₃O₄ NPs, biogas and CH₄ yield increased by 50%, 67%, and 70%, 116%, respectively, as compared to a control experiment. Farghali et al. (2019) used batch tests to assess the addition of Fe₂O₃ NPs to cattle manure at concentrations of 20 and 100 mg/L. When compared to the control condition, the aforementioned additions increased biogas and CH₄ yield by 9%, 11.1%, and 15.1%, 19.1%, respectively. Later, the same study compared different Fe (waste iron powder (WIPs) and Fe NPs) in the AD of cattle manure at different dosages (100, 500, and 1000 mg/L). According to the findings, the presence of Fe NPs increased CH₄ generation by 18.4–56.9% when compared to the control condition. Furthermore, they demonstrated WIPs advantage over Fe NPs interim CH₄ yields (Farghali et al. 2020). In another study (Juntupally et al. 2017), the addition of Fe₃O₄ NPs to biogas production was reported to increase it by 48.57%. According to Abdelwahab et al. (2021b), the addition of 15 mg/L Fe NPs increased biogas production by 64.10%, which is higher than the biogas production from sludge and slurry, which were 30.4% and 45.3%, respectively, with Fe NPs at 10 mg/L and 20 mg/L (Yu et al. 2016; Abdelsalam et al. 2017b). Furthermore, the addition of 30 mg/L Fe NPs increased cumulative CH₄ production by 118.8%, which is higher than sludge production, which was 43.5%, 40.4%, and 30% with 20 g/L, 1 g/L, and 11.6 g/L Fe NPs, respectively (Yu et al. 2016; Feng et al. 2014; He et al. 2017).

The presence of impurities in biogas, such as H₂S and CO₂, creates a slew of problems (Song et al. 2017; Sahota et al. 2018; Achinas et al. 2017). Depending on the substrate type, H₂S concentrations in biogas

range from 10 ppm to 10,000 ppm. Increased amounts of H₂S (200 ppm) in biogas (Lupitskyy et al. 2018) cause a number of issues, including injury to humans and livestock (Andriamanohiarisoamanana et al. 2015; Hu et al. 2018), and a reduction in biogas calorific value (Song et al. 2017; Sahota et al. 2018; Achinas et al. 2017).

To reduce the H₂S concentration in biogas, a variety of strategies have been used, including several well-known biological and chemical methods (Chaung et al. 2014; Pikaar et al. 2015). However, post-H₂S removal procedures are expensive, necessitate chemical handling, and lack long-term stability (Blazy et al. 2014). Due to its features such as strong reactivity and adsorption capacity, Fe NPs additives are promising adsorbents (Li et al. 2007; Han and Yan, 2016). Farghali et al. (2019) focused on the impact of Fe₂O₃ NPs on H₂S production from cattle manure AD. In comparison to the control condition, the addition of 20 and 100 mg/L Fe₂O₃ NPs reduced H₂S generation by 53.02 and 57.93%, respectively.

Farghali et al. (2020) concluded that adding 100, 500, and 1000 mg/L Fe₂O₃ NPs to the AD of cattle manure reduced H₂S production by 33.59%, 46.30%, and 53.52%, respectively, as compared to the control condition. In another study, adding 2000 and 8000 mg/L iron powder to AD of cattle manure reduced H₂S production by 93% and 99%, respectively, as compared to the control setup (Andriamanohiarisoamanana et al. 2018). Later, Abdelwahab et al. (2021b) found that compared to cattle manure-only, the cumulative H₂S production of 15, 30, and 60 mg/L Fe NPs was reduced by 81.8%, 93%, and 110.5%, respectively. Su et al. (2013) reported that 0.1 wt.% Fe NPs (size, 20 nm) reduced H₂S generation by 98%. There were no significant variations in H₂S yield across all Fe NP concentrations (p-value = 0.218–0.316). Furthermore, as Fe NPs concentrations increased, H₂S removal efficiency increased as well, with the largest increase occurring at 60 mg/L Fe NPs concentration (52.5%). Andriamanohiarisoamanana et al. (2018) reported a 93.3–99% increase in H₂S removal effectiveness in the concentration range of 2–20 g/L waste iron powder. These results suggested that a rise in H₂S reduction could be due to Fe²⁺ produced from Fe interacting with S²⁻ during Sulfate-Reducing Bacteria inhibition during the AD process, resulting in a decrease in H₂S generation (Andriamanohiarisoamanana et al. 2018).

2.2 Influences of iron nanoparticles on fundamental mechanisms of anaerobic digestion process

VFAs, pH, TA, TS, and VS are all important parameters that influence the fermentation process, according to Suanon et al. (2017). To begin with, VFAs with short carboxylic chains (C₂-C₆) are a significant intermediate product in the progression of AD (Kim et al. 2018; Meng et al. 2013; Wan et al. 2013). During the AD of cattle manure, Farghali et al. (2019) investigated the effect of Fe₂O₃ NPs on VFA content at two concentrations of 20 mg/L and 100 mg/L. The results indicated that there was no significant change in VFAs after treatment with both Fe₂O₃ NP concentrations compared to the control. During the 30-day fermentation period, however, the CH₄ levels for the aforementioned additives were 55.97% and 58.86%, respectively, compared to 53.68% for the control, indicating that the Fe₂O₃ NPs may have accelerated the utilization of VFAs, resulting in higher CH₄ production (Noonari et al. 2019; Farghali et al. 2020).

Ugwu and Enweremadu, (2020a) and Abdelwahab et al. (2020b) indicated that pH and total alkalinity (TA) are essential components during the AD process, and that monitoring their values is necessary to ensure the stability of the AD process as well as the preservation of optimal metabolic status. The recommended pH range for AD microbial growth is 6.8–7.2 (Ogejo et al. 2009). When Fe NPs are dissolved in an aqueous solution, pH influences the availability of iron ions (Eljamal et al. 2018, 2020). Furthermore, the size and concentration of Fe NPs, as well as the substrate being digested, influence the dynamic shift in pH during AD (Eljamal et al. 2018, 2020; Amen et al. 2017, 2018; Suanon et al. 2017). According to Amen et al. (2018), Suanon et al. (2017), and Abdelwahab et al. (2020b), the pH rose at the start of the AD and then fell, but did not fall below 7.0 until the process was completed. According to the authors, Fe NPs additions might have increased pH at the start of the AD in two ways: i) Fe NPs were oxidised to Fe^{+2} according to Eq. (1); and ii) the reaction between Fe NPs and organic substances such as CO_2 could have increased pH according to Eq. (2) (Chen et al. 2008). The pH variations, on the other hand, have a direct impact on TA concentration during AD. According to Abdelwahab et al. (2020b), the average TA concentrations were 4643, 4756, 4581, and 4518 mg CaCO_3/L , respectively, with Fe NPs added at 15, 30, 60 mg/L and control. A rise in TA concentration was found in the substrate treated with 30 mg/L Fe NPs. Suanon et al. (2017) found that the TA concentration indicated the consumption of VFAs by methanogen bacteria, which resulted in increased CH_4 generation (Chen et al. 2008).

The reduction of the solid during AD is the result of the organic matter degradation by microbes. It is expressed as either TS or VS removed (Ugwu and Enweremadu, 2020b). Abdelsalam et al. (2017b) studied the impact of three dosages of Fe NPs (5, 10, and 20 mg/L) on the TS and VS removal efficiency using cattle manure. When the substrate was treated with 20 mg/L Fe NPs, the maximum TS and VS removal performance was observed, with 25% and 20%, respectively, at the end of the experiment. Similarly, Farghali et al. (2019) studied the effect of the addition of Fe_2O_3 NPs on the TS and VS removal efficiency and found that the VS removal efficiency of 20 and 100 mg/L Fe_2O_3 NPs were 49.0% and 54.5%, respectively. However, no significant difference is reported on the TS removal efficiency. Moreover, the TS and VS removal efficiency increased by increased concentration of Fe NPs. While Abdelsalam et al. (2016) found that the TS and VS removal efficiency was increased by 30% and 23%, respectively when the substrate (cattle manure) was treated with 20 mg/L Fe_3O_4 NPs. Farghali et al. (2020) found that the TS and VS removal efficiency were increased by 66% and 50.31%, respectively when the substrate (cattle manure) was treated with 500 mg/L Fe_3O_4 NPs. Abdelwahab et al. (2020b) found that TS removal efficiencies of control, 15, 30, and 60 mg/L Fe NPs were 12.0%, 25.6%, 24.0%, and 20.7%, respectively. These findings agree with Ali et al. (2019) who found that the TS removal efficiency of control (municipal solid waste-only), 50, 75, 100, and 125 mg/L Fe_3O_4 were 19.2%, 38.2%, 50.3%, 29.4%, and 27.4%, respectively. Moreover, the VS removal efficiency for control, 15, 30, and 60 mg/L Fe NPs were 7.2%, 10.5%, 9.9%, and 9.6%, respectively. These findings are consistent with those of Farghali et al. (2019) who found that the VS removal efficiency of control, 20, and 100 mg/L Fe_2O_3 were 47.38%, 49.0%, and 54.5%, respectively. The changes of TS and VS contents with the use of Fe NPs indicated that Fe NPs increased

the rate of decomposition of organic materials by improving the capacity of methanogens bacteria to degrade organics.

2.3 Fertility evaluation of effluent containing iron nanoparticles

Microbial degradation during digestion enhanced the availability of nitrogen (N), phosphorous (P), and potassium (K) in organic material, allowing the effluent to be used directly as fertilizer or as an effective component of commercial fertilizers (Jeon et al. 2020; Yun et al. 2021). NPK organic compound fertilizers can significantly improve soil physio-chemical characteristics, boosting the formation of soil aggregate structure and increasing the activation of soil nutrients (Möller and Müller 2012). The effluent NPK content was evaluated for different Fe NPs concentrations to examine the practicality of employing effluent containing Fe NPs as fertilizers. The effluent NPK content was 5.84%, 5.70%, and 5.90%, respectively, with 15, 30, and 60 mg/L Fe NPs (Abdelwahab 2021). Because the NPK level of all Fe NPs effluents was near to the NPK content of bioorganic fertilizers, these effluents can be employed as efficient and promising organic fertilizer components.

3. Nickel Nanoparticles

During the AD process, the bacteria utilize Ni as a track element (Ajay et al. 2020). Many hydrogenases require Ni to function, therefore it's crucial for both acidogenic and methanogenic bacteria (Vignais and Billoud 2007). Ni plays a role in the expression of enzymes such as CO dehydrogenase/acetyl-CoA synthase (Methanogens/Homoacetogens) and Methyl-CoM-reducates (Methanogens) (Fournier and Gogarten, 2008; Ko et al. 2018; Romero-Güiza et al. 2016). Ni is also found in cofactor F430 (Prakash et al. 2014), which is necessary for the function of the methyl reductases complex, which catalyses the final step in the methane formation process (Thauer et al. 2008; Chen et al. 2016).

3.1 Impacts of nickel nanoparticles on gas yield

Abdelsalam et al. (2017a) studied the influence of Ni NPs on biogas and CH₄ production using cattle manure at a mesophilic temperature (37 ± 0.5°C). They confirmed that Ni NPs have a positive effect on cattle manure at the studied concentration (0.5-2 mg/L) by achieving a 46.4–74.2% greater biogas yield in AD, as well as a 49.0-100% higher CH₄ yield than in the control experiment. Furthermore, when the equivalent dosage of Ni NPs increased, the biogas production also increased, reaching 486.7, 503.3, and 520 mL biogas on the first day, respectively, when the cattle dung was exposed to 0.5, 1, and 2 mg/L Ni NPs. The lag phase in the control experiment (cattle manure only) lasted 11 days, yielding just 416.7 mL biogas. These findings are consistent with those of Abdelsalam et al. (2016), who found that when cattle manure was exposed to 2 mg/L Ni NPs, the highest biogas startup was obtained, yielding 658 mL biogas (on average over the first five days of digestion), while 1 mg/L Co NPs, 20 mg/L Fe NPs, and 20 mg/L Fe₃O₄ NPs yielded 596, 580, and 633.3mL biogas, respectively.

During the AD process, the concentration of Ni NPs and the substrate type are critical variables (Abdelsalam et al. 2016, 2017b). Hassanein et al. (2019) investigated the influence of Ni NPs on CH₄ generation from poultry litter at three doses of 3, 6, and 12 mg/L Ni NPs. The addition of 12 mg/L Ni NPs boosted CH₄ production by 38.48%, resulting in 261 mL CH₄ /g VS during the first ten days vs the same CH₄ /g Versus production over 69 days in the control experiment. In addition, 95.1% of the CH₄ from Ni NPs (12 mg/L) was generated within the first 29 days. Similarly, Abdelwahab et al. (2021a) discovered that adding 1, 2, and 4 mg/L of Ni NPs to cattle manure enhanced CH₄ output by 17.32%, 70.46%, and 53.79%, respectively, as compared to cattle manure only. He et al. (2019) investigated the effect of Ni NPs on CH₄ generation from sludge. Ni NPs were applied at four different dosages: 1, 50, 200, and 600 mg/g-TSS (total suspended solids). The presence of 1 mg/g-TSS Ni NPs had no effect on CH₄ yield, according to the findings. The effects of Ni NPs on the CH₄ yield were negative as the dosage of Ni NPs was increased to 50 mg/g-TSS and above. When the substrates were treated with 50, 200, and 600 mg/g-TSS, the CH₄ yield was reduced by 89.3%, 84.3%, and 56.4%, respectively.

Hassanein et al. (2019) evaluated the impact of three concentrations of Ni NPs (3, 6, and 12 Ni NPs) on the cumulative H₂S production of poultry litter to determine the impact of Ni NPs on impurities such as H₂S and CO₂ in the biogas. When the substrate was treated with 6 mg/L Ni NPs, there was no significant difference in H₂S production when compared to the control condition (poultry litter only). While treated the substrate with 12 mg/L Ni NPs a negative effect on H₂S yield (10.7% increase) has been obtained. When the substrate was exposed to 3 mg/L Ni NPs, there was a positive effect on H₂S production (5.9% decrease). In another study, Abdelwahab et al. (2021a) found that 2 mg/L Ni NPs added to the solution resulted in a 47.5% H₂S removal effectiveness. The removal efficiency of Ni NPs at 1 and 4 mg/L was 14.16% and 34.16%, respectively.

3.2 Impacts of nickel nanoparticles on fundamental mechanisms of anaerobic digestion process

Tsapekos et al. (2018) studied the influence of Ni NPs on pH, TA, and VFAs during the AD of sewage sludge at two concentrations (5 and 10 mg/Kg VS) using the batch system, focusing on the effect of Ni NPs on the AD process stability. To begin with, neither treatment's pH nor TA values differed significantly from the control. The lack of substantial differences, according to the authors, may be attributable to the use of a large volume of anaerobic inoculum (Tsapekos et al. 2018). In addition, there was a clear difference in the accumulation of VFAs. When the substrates were treated with 5 and 10 mg Ni NPs/Kg VS, respectively, VFAs in the form of acetate in (mg/L) were degraded by 1.39 and 1.38 times, respectively, compared to an untreated substrate (control). Abdelsalam et al. (2017a) studied the influence of three different Ni NP concentrations (0.5, 1, and 2 mg/L) on the redaction of the TS and VS during the AD of cattle manure. When the substrate was exposed to 2 mg/L Ni NPs, the maximum TS and VS removal efficiency were attained, with 33.3% and 26.3%, respectively, at the end of the experiment. In another study, Abdelsalam et al. (2016) found that when the substrate (cattle manure) was treated with 2 mg/L Ni NPs, the maximum TS and VS removal efficiency was attained, with 28.0% and 20.4%,

respectively. While the removal efficiency of 1 mg/L Co NPs and 20 mg/L Fe NPs in TS and VS was 10.3% and 14.2%, respectively, the removal efficiency of 1 mg/L Co NPs and 20 mg/L Fe NPs was 23% and 20.4%. These findings corroborate those of Abdelwahab et al. (2021a), who found that the TS removal efficiencies of cattle manure-only, 1, 2, and 4 mg/L Ni NPs were 12.0%, 17.7%, 19.2%, and 16.2%, respectively. Furthermore, the VS removal efficiencies of cattle manure-only, 1, 2, and 4 mg/L Ni NPs were 7.2, 11.5, 12.1, and 10.6%, respectively.

3.3 Fertility evaluation of effluent containing nickel nanoparticles

The digestates included 5.94%, 5.88%, and 5.86% NPK for Ni NPs at 1, 2, and 4 mg/L, respectively, according to Abdelwahab et al. (2021a). According to the Indian Institute of Soil Science and the Indian Council of Agricultural Research, bioorganic fertilizers should have an NPK concentration of more than 5%. As a result, the organic fertilizer components in these digestates are outstanding. Furthermore, digestates had nutritional values comparable to commercial bioorganic fertilizers and a higher TN than commercial bioorganic fertilizers. This suggests that these digestates are well-suited to soils with low nitrogen levels. The TK content of these digestates, on the other hand, was lower than that of commercial bio-organic fertilizer; this finding was consistent with the fertility test results of other cattle dung digestates (Li et al. 2018; Zhang et al. 2018).

4. Cobalt Nanoparticles

During the AD process, cobalt (Co) has proved to be a significant trace mineral for the growth of methanogenic bacteria (Ajay et al. 2020). Cobalt is required for methanogenic bacteria to degrade methanol (as a protein cofactor of vitamin) (Roussel, 2013). In addition, the usage of Co is thought to be a significant element in the oxidation of acetate to CO₂ and H₂, resulting in the hydrogenotrophic methanogenic process (Thauer et al. 2008; Romero-Güiza et al. 2016).

4.1 Effects of cobalt nanoparticles on gas yield

Abdelsalam et al. (2016) studied the impact of Co NPs (20 nm) on biogas and CH₄ production from cattle manure slurry using a batch AD system. Treatment of the substrate with 0.5 and 1 mg/L Co NPs increased cumulative biogas production by 36.5% and 64.12%, respectively) as compared to the control. These findings are consistent with those of Zaidi et al. (2018), who reported that using 1 mg/L Co NPs during the AD of green microalgae boosted biogas generation by 9% over a control experiment. Furthermore, the aforementioned shorten the time it takes to reach peak biogas and CH₄ production. However, compared to the control condition, the addition of 2 mg/L Co NPs reduced both biogas and CH₄ production by 5.2% and 14.54%, respectively. Poultry litter containing 1.4, 2.7, or 5.4 mg/L Co NPs improved CH₄ output by 29.0%, 26.05%, and 30%, respectively (Hassanein et al. 2019). Another study used cattle manure as a substrate to investigate the impact of 1 mg/L Co NPs in AD. Biogas and CH₄

production have increased by 71.2% and 45.9%, respectively, as compared to control (Abdelsalam et al. 2016).

When compared to cattle-dung only, Abdelwhab et al. (2021b) found that the presence of 1 and 2 mg/L Co NPs increased cumulative biogas yield by 6.83% and 14.81%, respectively ($p < 0.05$). However, there were no significant changes in cumulative biogas generation with 3 mg/L Co NPs compared to cattle manure alone (p -value = 0.430). When compared to cattle manure -only, the addition of 1, 2, and 3 mg/L of Co NPs increased CH_4 yield by 79.12%, 56.37%, and 54.65%, respectively ($p < 0.05$). Furthermore, no significant differences in CH_4 yield were observed when 2 mg/L Co NPs and 3 mg/L Co NPs were added to the substrate (p -value = 0.857). These findings support those of reported by Zandvoort et al. (2006), who discovered that 0.8 mg/L Co is the best dose. Furthermore, when the substrate was exposed to 1 mg/L Co NPs, the maximum CH_4 yield was achieved, which accords with Abdelsalam et al. (2016), who reported that the presence of 1 mg/L Co NPs boosted CH_4 production by 86% when compared to the control condition (manure without NP additives). Furthermore, the increase in CH_4 produced by 1 mg/L Co was consistent with the findings of Qiang et al. (2012), Demirel and Scherer (2011), and Feng et al. (2010), all of whom concluded that Co is an essential metal for methanogenesis because it acts as a metallic enzyme activator.

Hassanein et al. (2019) used poultry litter in a mesophilic condition to investigate the effects of Co NPs on H_2S production in biogas and AD process stability. They found that at the studied concentration range (2.7–5.4 mg/L Co NPs), Co NPs have a positive impact on H_2S production, with H_2S production being 5.93–8.19% than in the control condition. However, no significant difference in H_2S production was found when the substrate was treated with 1.4 mg/L Co NPs compared to the control setup. Another study, Abdelwahab et al. (2021b) found that cumulative H_2S production of 1, 2, and 3 mg/L Co NPs was reduced by 15.38%, 13.20%, and 57.89%, respectively, when compared to cattle manure-only. With 3 mg/L Co NPs added, the maximum H_2S removal efficiency of 57.89% was obtained. Co NPs had a clearance efficiency of 15.38% at 1 mg/L and 13.20% at 2 mg/L.

4.2 Effects of cobalt nanoparticles on fundamental mechanisms of anaerobic digestion process

Zaidi et al. (2018) studied the effect of 1 mg/L Co NPs on VFAs production during the AD of microalgal biomass after a 170h fermentation period, focusing on VFAs production, TS and VS decomposition during the fermentation process. The addition of 1 mg/L Co NPs boosted VFA production substantially. These findings corroborate those of Gustavsson et al. (2013), who discovered that adding Co to sulfur-rich stillage during AD increased VFAs. Abdelsalam et al. (2017b) investigated the effect of Co NPs in the 0.5-2 mg/L concentration range on the elimination effectiveness of TS and VS in cattle dung. When the substrate was treated with 1 mg/L Co NPs, the highest TS and VS removal efficiency was attained at the end of the experiment, and were 12.9% and 17.0%, respectively. These findings are consistent with those reported by Abdelsalam et al. (2016), who reported that adding 1 mg/L Co NPs enhanced the removal

efficiency of TS and VS by 10.3% and 14.2%, respectively. Co nanoparticles increased the degradation of organic matter by boosting the capacity of methanogens bacteria to breakdown organics, as evidenced by the change in TS and VS content after the addition of Co NPs. Abdelwhab et al. (2021b) found that TS removal efficiency of cattle manure-only, 1, 2, and 3 mg/L Ni NPs are calculated to be 12.04%, 14.81%, 16.25%, and 14.81%, respectively. moreover, Cattle manure-only, 1, 2, and 3 mg/L Co NPs have VS removal efficiencies of 11.55%, 12.16%, 11.85%, and 10.66%, respectively.

4.3 Fertility evaluation of effluent containing cobalt nanoparticles

Abdelwahab et al. (2021b) found that the total nutritional (NPK) content of the digestate with 1, 2, and 3 mg/L Co NPs is 5.32%, 4.68%, and 4.63%, respectively. Because all Co NPs concentrations had a total nutrient content of close to 5%, they can be utilized in combination with an artificial compound fertilizer. The digestates were dewatered and dried to provide a high-quality organic compound fertilizer. The physical and chemical features of soil can be improved with NPK organic compound fertilizer, which promotes the creation of soil aggregate structure and increases the activation of soil nutrients. It is obvious that when NPK organic compound fertilizer is employed, the crops demand significantly less water, and the area's chronic water shortage problem may be remedied. As a result, the AD digestate can be combined with the three Co NPs to create an NPK organic compound fertilizer that benefits plant height, root length, root diameter, and dry weight (Möller K and Müller 2012).

5. Challenges And Future Studies

The addition of various dosages of NPs promotes anaerobic bacterial and Archaeal activity, as well as the degradation of organic matter. However, accumulative residual toxicity in soils, such an application method may cause some environmental concern due to their toxicity to bacteria in manure, soil, and neighbouring ecosystems. A lot more research is needed to be sure there aren't any negative effects on the environment when using additives like Fe, Ni, and Co NPs in large-scale AD systems. This includes looking into how the NPs might affect their environment, the field where the digester effluent is applied, and the crops that are grown for humans and animals.

6. Conclusions

The supplementation of Fe, Ni, and Co NPs to the AD system has a huge effect on the performance of the AD system in terms of gas yield and process stability. Furthermore, the effluent from AD systems when using Fe, Ni, and Co NPs has greater TN, TP, and TK concentrations which may be employed as a component of bioorganic fertilizer. The use of Fe, Ni, and Co NPs in the AD system for the treatment of organic waste increases the use of waste biomass and effluent.

Declarations

Acknowledgments

The authors gratefully acknowledge the financial support of Al-Azhar University, Cairo, Egypt.

Authors' contributions

TAM Abdelwahab contributed to background, iron, and nickel nanoparticles sections. AEM Fodah contributed to nickel and cobalt nanoparticles sections. All authors read and approved the final manuscript.

Funding

Al-Azhar University, Cairo, Egypt.

Availability of data and materials

None.

Ethics approval and consent to participate

All the authors abide by the ethics rules of the journal.

Consent for publication

All the authors approve this manuscript for publication.

Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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