Review Paper

Utilization of nanoparticles for biogas production focusing on process stability and effluent quality

Taha Abdelfattah Mohammed Abdelwahab[1] · **Ahmed Elsayed Mahmoud Fodah**[1]

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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. Several issues have been raised related to the effectiveness of the anaerobic digestion process in recent years. Hence nanoparticles (NPs) have been used widely in anaerobic digestion 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 anaerobic digestion process using single and combinations nanoparticle. In summary, the utilization of NPs have beneficial effects on CH_4 production, 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 H_2S production than increasing CH_4, whereas Ni NPs and Co NPs at concentrations greater than 2 mg/L and 1 mg/L, respectively, reduce CH_4 production. Effluent with Fe and Ni NPs showed stronger fertilizer values more than Co NPs. Fe/Ni/Co NP combinations are more efficient in enhancing CH_4 production than single NPs. Therefore, it is possible to utilize NPs combinations as additives to improve the effectiveness of anaerobic digestion.

Article highlights

- Single NPs (e.g., Fe, Ni, and Co NPs) in low concentrations are more effective in increasing CH_4 production than reducing H_2S production.
- Optimal Fe, Ni, and Co NP concentrations enhance anaerobic digestion process performance.
- Addition of Fe, Ni, and Co NPs above tolerated concentration causes irreversible inhibition in anaerobic digestion.
- Effluent with Fe, Ni, and Co NPs showed stronger fertilizer values.
- Nanoparticle combinations are more effective for increasing the CH_4 production than signal NPs.

Keywords Anaerobic digestion · Metallic nanoparticles · Metal oxides nanomaterial · Nanoparticle combinations · Cattle manure treatment · Effluent

Abbreviations

WBA	World Bioenergy Association
WHO	World Health Organization
N	Nitrogen
ppm	Parts per million
S	Sulfide

✉ Taha Abdelfattah Mohammed Abdelwahab, tahaabdelfattah@azhar.edu.eg; ✉ Ahmed Elsayed Mahmoud Fodah, ahmedfodah@azhar.edu.eg | [1]Faculty of Agricultural Engineering, Al-Azhar University, Cairo 11751, Egypt.

CO_2	Carbon dioxide
TA	Total alkalinity
P	Phosphor
H_2S	Hydrogen sulfide
VS	Volatile solids
K	Potassium
CH_4	Methane
TS	Total solids
WIPs	Waste iron powder
nm	Nanometer
TSS	Total suspended solids
TN	Total nitrogen
NPs	Nanoparticles
H_2O	Water
TK	Total potassium
Fe	Iron
VFAs	Volatile fatty acids
°C	Degree celsius
Ni	Nickel
H_2	Hydrogen
%	Percentage
Co	Cobalt
IEA	International Energy Agency
NPK	Nitrogen, phosphorus, potassium
BTOE	Billion tons oil equivalents

1 Introduction

Energy "powers" the suitable light and temperatures in our homes and workplaces; it fuels manufacturing facilities, urban infrastructure, and the numerous technological aids we use on a daily basis; and it enables us to travel virtually endlessly [1, 2]. The shortage of fossil fuels such crude oil, coal, and natural gas, as well as the excessive gas emissions caused by the over use of fossil fuels, are the present global energy concerns that are causing tremendous worry [3].

From 14,000 BTOE (billion tonnes of oil equivalent) now to more than 18,000 BTOE by 2030, the world's energy consumption is rising quickly. It's also important to note that global energy consumption increased for natural gas, oil, and coal by 5.3%, 1.5%, and 1.4%, respectively [4]. The International Energy Agency [3] estimates that by 2050, global energy consumption may increase by three times its level from the previous year.

Additionally, the use of fossil fuels has contributed to air pollution, global warming, and climate change [5–9]. Finding a new clean and sustainable energy source is the only solution to the environmental crisis brought on by growing CO_2 emissions and declining fossil fuel supply. There is a movement in support of renewable energy sources over fossil fuels [10–16].

About 17.8% of the world's energy demand is fulfilled by renewable energy sources such biomass, hydropower, wind, sun, geothermal, and tide [17]. Biomass and organic wastes are better renewable energy sources than fossil fuels in terms of waste management and reducing environmental impact [18].

Some of the wastes that can be used as feedstock include animal manure [19], agricultural residues [20], food wastes [21], sewage sludge [22], and other energy crops [23]. Livestock covers up around 40% of the worldwide value of agricultural products, including animal manure [24]. To fulfil the rising demand for dairy and meat products, traditional scattered family-scale livestock farms have been gradually transformed into centralized ones in recent years [25]. Cattle, swine, poultry, and sheep farms all create a significant amount of manure that needs to be properly managed [26].

More than half of all generated manure comes from cattle, and that percentage is expected to increase to more than 75% during the next ten years [27, 28]. More than 50% of the total solids in cattle manure are made up of undigested lignocellulosic materials such cellulose, hemicellulose, and lignin [29–35].

In the absence of oxygen, anaerobic digestion utilizes the activity of bacteria to transform organic waste into sustainable energy in the form of methane (CH_4)-enriched biogas and effluent [36–38]. With trace levels of additional impurities like H_2O (5–10%) and H_2S (1–10,000 ppm), biogas generally contains a ratio of 40–75% CH_4 and 25–60% CO_2 [39].

Biogas with a high CH_4 concentration has a heat value in the 20–25 MJ/m^3 range. In addition to reducing the use of traditional energy sources, biogas also reduces greenhouse gas emissions by around 80% [40]. This makes it an excellent substitute for fossil fuels. Additionally, substituting effluent for inorganic mineral fertilizer might reduce the need for fossil fuels and the risk of contamination [41, 42].

There are numerous techniques to make cattle manure receptive to anaerobic microorganisms. Including co-digestion with other wastes [43–47], pretreatments (chemical, ultrasonic, and thermal) [46–49], and the design of bioreactors and the optimization of operation parameters. Careful material selection is necessary for chemical pretreatment in order to prevent hazardous processes [50, 51]. Additionally, heat and ultrasonic treatments can cause considerable losses of carbohydrates, bringing down sugar levels. To achieve the optimum particle size reduction, physical pretreatment also requires a significant amount of energy [52].

Inorganic and organic additives [53–55], including green biomass and enzymes, are both used to increase CH_4 production in anaerobic digestion processes.

Macronutrients and micronutrients are the two categories into which inorganic additions are divided [56]. The anaerobic digestion process substrate is supplemented with macronutrients (i.e., P, N, and S) in the form of salts to increase the system buffer capacity and sustain microorganism activity [57]. But a large dosage of bulk materials can be hazardous to anaerobic microbes, and they might not biodegrade properly during digestion [58]. Salts, bulk materials, and more recently nanoparticles (NPs) are used to add micronutrients (Fe, Ni, and Co) to the anaerobic digestion feedstock [59, 60].

NPs are three-dimensional particles that have a size between 1 and 100 nm [61]. NPs are categorised using their chemical components, dimensions, appearance, condition, and place of origin [62–65]. Their size, which in at least one dimension ranges from 1 to 100 nm [66], is another factor used to classify them. In general, NPs contain a large number of particles per unit weight, a high surface-to-volume ratio, and confinement or quantum effects, which means fewer atoms per particle. These NPs specific traits lead to properties that are significantly different from those of the same material when it is in its bulk state [66].

In reality, the majority of NPs have the ability to bind to and maintain inhibitory elements such heavy metals on their surfaces [37, 67]. NPs (such as Fe, Ni, Co, and metal oxides) promote the activation of microorganisms and important enzymes, increasing the production of biogas and CH_4, and decreasing the concentration of H_2S [68–71].

Hence, this review aims to provide insights to the influences released by single NP (e.g. Fe, Ni, Co, metal oxides) and NP combinations on cattle manure anaerobic digestion process in terms of gas yield (CH_4, CO_2, and H_2S), their influences on fundamental mechanisms such as pH, volatile fatty acids (VFAs) and total alkalinity (TA) concentration, total solids (TS) and volatile solids (VS) degradation, as well as their influences on fertility evaluation of the effluent. Finally, perspective on the required future trends and research on the application of NPs in the anaerobic digestion process are highlighted.

In this review, the first three sections [3–5] discuss the effects of single NPs (such as Fe, No, and Co) on gas yield and the stability of the anaerobic digestion process. For clarity of reading, the data from these sections were compiled into Tables 1, 2, and 3. The effects of NP combinations on the stability of the overall anaerobic digestion process and the effluent fertility evaluation are shown in Sect. 6. For clarity of reading, the data from Sect. 6 was summarized into Table 4. The comparative research between single and combination NPs on average CH_4 generation rate as well as effluent quality from anaerobic digestion of cattle manure was discussed in the reviews at the end.

2 Iron nanoparticles

Iron (Fe) NPs are one of the most often used additives for enhancing anerobic digestion performance because of their conductive properties and low price. Fe NPs of various sorts have been demonstrated to stimulate anerobic digestion [25]. One of the many varieties of Fe NPs that contribute to accelerating the anerobic digestion process is zero-valent iron NPs. In general, it has the ability to serve as an electron donor, release Fe 2+ into the anaerobic system, assist in the creation of vital enzymes, enhance total hydrogen

Table 1 Effects of iron nanoparticles on the performance of biogas production process and effluent quality

NPs type	NPs Size, nm	Concentrations of NPs	Substrate type	HRT, day	Temperature (°C)	Main effect	Reference
Fe_3O_4	7	20 mg/L	Cattle manure	40	37	667 ml Biogas production during the first 6 days compared to same production over 40 days in control	[70]
Fe_2O_3	20–40	20 and 100 mg/L	Cattle manure	30	38	Reduce the time required to achieve the highest biogas production compared with the control	[72]
	40	1500 mg/L	Cattle manure	200 h	30	Not inhibitory the methanogens bacteria	[73]
Fe	9	5 mg/L 10 mg/L 20 mg/L	Cattle manure	50	37	45% increase in biogas production, 59% increase in methane production	[58, 71]
Fe_3O_4	20–40	100 mg/L	Cattle manure	30	38	CH_4 formation rate increase by 19.74%	[50]
Fe_2O_3	20–40	20 mg/L	Cattle manure	12	38	CH_4 formation rate increase by 22.40%	[73]
Fe	435.1	15–60	Cattle manure	30	37	118.8% Increased in CH_4 yield, 81–110% Decrease in H_2S production rate, and improved the effluent quality compared with control	[74]

Table 2 Effects of nickel nanoparticles on the performance of biogas production process and effluent quality

NPs type	NPs Size, nm	Concentrations of NPs	Substrate type	HRT, day	Temperature (°C)	Main effect	Reference
Ni	7–9	20 mg/L	Cattle manure	50	37	Highest CH_4 percent by 72%	[71]
	160	0.1 wW	Sludge	30	37	25.2% Increased CH_4 yield	[75]
	50–70	1500 mg/L	Sludge	30		29.55% Increased biogas yield	[34]
	30–80	12 mg/L	Poultry litter	69	–	10.7% Decreased H_2S production	[76]
	17	2 mg/L	Cattle manure	40	37	667 ml Biogas production during first 5 days compared to same production over 40 days in control	[70]
	20	2 mg/L	Cattle manure	50	37	74.2% Increased in specific biogas production	[70]
	-	200 mg/g-TSS	Sludge	12	35	96% Decreased CH_4 volume	[77]
	100	5–10 mg/KgVS	Sludge	–	37	Increase methane production up to 10%	[78]
	65–114	1–4 mg/L	Cattle manure	30	37	70.46% Increase CH4 production, 90.47% Decreased H2s yield, and stronger fertilizer values	[79]

Table 3 Effects of cobalt nanoparticles on the performance of biogas production process and effluent quality

NPs type	NPs Size, nm	Concentrations of NPs	Substrate type	HRT, day	Temperature (°C)	Main effect	Reference
Co	20	2 mg/L	Cattle manure	50	37	74.2% Increased in specific biogas production	[71]
	–	200 mg/g-TSS	Sludge	12	35	96% Decreased CH_4 volume	[80]
	30–80	5.7 mg/L	Poultry litter	69	–	6.3% Decreased H_2S production	[76]
	28	1 mg/L	Cattle manure	40	37	667 ml Biogas production during first 7 days compared to same production over 40 days in control	[70]
	20	2 mg/L	Cattle manure	50	37	14% Decreased in specific CH_4 production	[58]
	70–104	1–3 mg/L	Cattle manure	30	37	Improved the hydrolysis rate by 66.66–144%, the effluent with Co NPs showed remarkable fertility	[81]

methanogen consumption, change the type of hydrolysis fermentation, and increase acetic acid content [75, 84–86].

To start, the mechanism of Fe NPs in anerobic digestion is that they release two electrons, Eq. (1), upon oxidation. The hydrogenation process is favored by the anaerobic circumstances created by the electron releases. Inorganic CO_2 Eq. (2) or acids Eq. (3) can also absorb it to boost CH_4 production. In addition, corrosion can convert Fe NPs to H_2 (4). H_2 is necessary for the conversion of CO_2 during methanogenesis [87].

$$Fe^0 \rightarrow Fe^{2+} + 2e^- \quad (1)$$

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O \quad (2)$$

$$4CH_3COOH \rightarrow CH_4 + CO_2 \quad (3)$$

$$Fe^0 + H_20 \rightarrow Fe^{2+} + H_2 + 2OH^- \quad (4)$$

2.1 Influences of iron nanoparticles on gas yield

Table 1 presents the effects of iron (Fe) nanoparticles on the performance of the biogas production process and effluent quality under different process conditions. It is clearly seen that the Fe NPs can be used in the form of Fe, Fe_2O_3, and Fe_3O_4 where their effect varies according to NPs concentration, size, process temperature, and substrate type. The possible reason for that is the difference in the

Table 4 Effects of nanoparticle combinations on the performance of biogas production process and effluent quality

NPs type	NPs Size, nm	Concentration of NP combinations	Substrate type	HRT, day	Temperature (°C)	Effect	Reference
Fe_2O_3 and TiO_2	25	100 mg/L Fe_2O_3 + 500 mg/L TiO_2	Cattle manure	30	38	62% H_2S reduction efficiency	[72]
		20 mg/L Fe_2O_3 + 500 mg/L TiO_2				54% H_2S reduction efficiency	[72]
Fe, Ni, and Co	55	100 mg/L Fe + 12 mg/L Ni + 5.4 mg/L Co	Poultry litter	79	37	Not effect in CH_4 production	[76]
		200 mg/L Fe + 24 mg/L Ni + 10.8 mg/L Co				8.6% Increase CH_4 production	[76]
		400 mg/L Fe + 48 mg/L Ni + 21.6 mg/L Co				7.8% Increase CH_4 production	[76]
		1000 mg/L Fe + 120 mg/L Ni + 54 mg/L Co				Not effect in CH_4 production	[76]
nZVI and zeolite	45 nZVI, 7 µm zeolite	500 mg/L nZVI + 4 g/L zeolite	Domestic sludge	14	37	74% CH_4 content compared with 22% in control experiment	[82]
iron oxide and zeolite	20 nm iron oxide NPs coated on 0.5–1 mm zeolite	Provide (2 mM) 1120 mg/L Fe element	Cattle manure	–	35	372.85% increase in cumulative CH_4 production	[83]
Fe, Ni, Co	103–116 Fe NPs, 65–114 Ni NPs, 70–104 Co NPs	30 mg/L Fe NPs + 2 mg/L Ni NPs + 1 mg/L Co NPs	Cattle manure	15	37	14.61% increase in biogas production, 19.3% increase in CH_4 production, and H_2S production decreased by 35.01%	[69]

chemical composition of the substrate and the mechanism of the NPs applied.

For evaluating anaerobic digestion efficacy, biogas and CH_4 production are essential metrics [75, 88]. Abdelsalam et al. [71] examined the effect of Fe NPs on biogas production and CH_4 content using cattle manure at a mesophilic temperature (37 °C). By achieving a 44–45% higher biogas yield than the control (without additives) and a 37.6–59.5% higher CH_4 yield than the control, they showed that Fe NPs, at the observed concentrations (5–30 mg Fe NPs/L), had a beneficial effect on control. The authors claims that Fe NP additions might enhance CH_4 production in two different ways. Fe NPs initially helped with acetate synthesis. Second, in the conversion of CO_2 to CH_4, Fe NPs serve as electron donors.

When cattle manure was treated with 20 mg/L Fe NPs and 20 mg/L Fe_3O_4 NPs, biogas and CH_4 production increased by 50, 67 and 70, 116%, respectively, compared to a control experiment [70]. In order to evaluate the addition of Fe_2O_3 NPs to cattle manure at concentrations of 20 and 100 mg/L, Farghali et al. [72] utilised batch testing. The aforementioned changes enhanced the biogas and CH_4 yield by 9.0, 11.1%, and 15.1% and 19.1%, respectively, above the control condition.

Later, the same study examined various Fe (waste iron powder (WIPs) and Fe NPs) at various doses (100, 500, and 1000 mg/L) in the anaerobic digestion of cattle manure. The results showed that Fe NPs enhanced CH_4 production by 18.4–56.9% in comparison to the control condition. They also showed that WIP had an edge over interim CH_4 yields from Fe NPs [50]. According to another study by Juntupally et al. [89], the production of biogas was said to rise by 48.57% when Fe_3O_4 NPs were added. The biogas production from sludge and slurry was 30.4% and 45.3%, respectively, with Fe NPs at 10 mg/L and 20 mg/L, according to Abdelwahab et al. [74]. This is greater than the biogas production from sludge and slurry with Fe NPs at 15 mg/L, which was enhanced by 64.10%. Additionally, the addition of 30 mg/L Fe NPs enhanced cumulative CH_4 production by 118.8%, exceeding the 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 [77, 90, 91].

This showed that the addition of Fe NP additions increased the production of CH_4 by releasing two electrons as a result of oxidation to Fe + 2 under anaerobic conditions [92]. Inorganic CO_2 or acids may consume the electrons that Fe releases, accelerating the hydrogenation process and resulting in the production of additional CH_4 [93].

Numerous issues are brought on by the presence of impurities in biogas, such as H_2S and CO_2 [94–96]. H_2S concentrations in biogas range from 10 to 10,000 ppm, depending on the kind of substrate. Increased levels of H_2S (200 ppm) in biogas [94] result in a variety of problems, including harm to people and animals [35, 95] and a decrease in the calorific value of the fuel [94–96].

Several well-known biological and chemical techniques as well as other tactics have been utilized to lower the H_2S content in biogas [96, 97]. Post-H_2S removal techniques, however, are pricy, need for chemical handling, and lack long-term stability [98]. Fe NPs additives are potential adsorbents because of their qualities including high reactivity and adsorption capability [93, 99]. On the effect of Fe_2O_3 NPs on H_2S production from cattle manure anaerobic digestion, Farghali et al. [72] concentrated their attention. By adding 20 and 100 mg/L of Fe_2O_3 NPs, H_2S production was decreased by 53.02 and 57.93%, respectively, in contrast to the control condition.

Farghali et al. [50], adding 100, 500, and 1000 mg/L Fe_2O_3 NPs to the anaerobic digestion of cattle manure decreased H_2S production by 33.59%, 46.30%, and 53.52%, respectively, in comparison to the control condition. In a different investigation, the production of H_2S was decreased by 93 and 99%, respectively, when 2000 and 8000 mg/L iron powder were added to the anaerobic digestion of cattle manure [100]. Later research by Abdelwahab et al. [74] showed that the cumulative H_2S production of 15, 30, and 60 mg/L Fe NPs was reduced by 81.8%, 93%, and 110.5%, respectively, when compared to cattle manure alone. According to Su et al. [101], 0.1 wt.% Fe NPs (size, 20 nm) decreased H_2S production by 98%. Additionally, H_2S removal efficiency improved along with the rise in Fe NPs concentrations, peaking at 60 mg/L Fe NPs concentration (52.5%). In the concentration range of 2–20 g/L waste iron powder, Andriamanohiarisoamanana et al. [100] observed a 93.3–99% improvement in H_2S removal efficacy. These findings showed that a decrease in H_2S production during Sulfate-Reducing Bacteria suppression throughout the anaerobic digestion process, along with an increase in H_2S redaction, might be the cause [100].

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

Suanon et al. [75] state that VFAs, pH, TA, TS, and VS are all significant factors that affect the fermentation process. VFAs with short carboxylic chains (C2-C6) are an important intermediate product in the development of anaerobic digestion, to start [102–104]. Farghali et al. [72] examined the impact of Fe_2O_3 NPs on VFA content at two concentrations of 20 mg/L and 100 mg/L during the anaerobic digestion of cattle manure. According to the findings, neither of the Fe_2O_3 NP concentrations treated the VFAs significantly differently from the control. The CH_4 levels for the aforementioned additions were 55.97 and 58.86% throughout the 30-day fermentation period, compared to 53.68% for the control, indicating that the Fe_2O_3 NPs may have sped up the use of VFAs, leading to increased CH_4 production [50, 105].

The effect of Fe NPs on VFAs at three concentrations is investigated by Abdelwahab et al. [74]. The findings showed that there were three phases to the variation in VFAs. With the treatment with 60 mg/L Fe NPs and only cattle manure, the VFAs concentration initially exhibited a small rise trend over the first 10 days of the digestion period. This suggested that the application of Fe NPs at a concentration of 60 mg/L might modestly reduce the activity of hydrolyzed acidifying bacteria. In contrast to cattle manure alone, the presence of 15 and 30 mg/L of Fe NPs revealed a minor decreasing tendency. The VFAs content showed a fast downward trend in the second stage (days 10–20 of the digesting period) for all Fe NPs additions, with the maximum VFAs degradation of 2850 mg/L with 30 mg/L of Fe NPs.

These findings concur with those of Jia et al. [106], who found that throughout the experimental period, 500 mg/L Fe NPs temporarily reduce the concentration of VFAs for a period of time (35 days). This showed that i) the Fe NPs functioned as an efficient electron donor for microbial metabolism once microorganisms acclimated to the environment [90]; and (ii) the addition of trace elements like Fe may reduce the initial VFAs cumulation during the anaerobic digestion [107, 108]. The VFAs concentration increased with all Fe NP concentrations in the final stage (during the last 10 days of the digestion period), reaching its maximum value of 4050 mg/L for 15 mg/L Fe NPs. The reduction in total alkalinity may be the cause of the increase in VFAs in the final stage. The daily biogas production and pH value decreasing during the final stage may be related to the growth and accumulation of VFAs. The production of biogas and pH both decreased when VFAs concentrations rose and accumulated [83, 109].

According to Ugwu and Enweremadu, [110] and Abdelwahab et al. [74], pH and TA are crucial elements throughout the anaerobic digestion process, and it is important to monitor their levels in order to maintain both the stability of the anaerobic digestion process and good metabolic condition. 6.8–7.2 is the suggested pH range for anaerobic digestion microbiological development [111]. The availability of iron ions when Fe NPs are dissolved in an aqueous solution depends on pH [112, 113]. Additionally, the substrate being digested and the size and concentration of Fe NPs affect the dynamic shift in pH during anaerobic digestion [75, 82, 88, 112–114]. The pH increased at the beginning of the anaerobic digestion and gradually decreased, but it didn't drop below 7.0 until the process was finished [75, 88, 115]. The addition of Fe NPs, according to the authors, may have increased pH at the beginning of the anaerobic digestion in two different ways: first, according to Eq. (1), Fe NPs were oxidised to Fe+2; second, according to Eq. (2), the reaction between Fe NPs and organic substances, like CO_2, may have increased pH [114].

On the other hand, the fluctuations in pH have a direct effect on the level of TA during anaerobic digestion. The average TA concentrations were 4643, 4756, 4581, and 4518 mg $CaCo_3$/L, respectively, according to Abdelwahab et al. [74], with Fe NPs added at 15, 30, and 60 mg/L and control. The substrate that had been treated with 30 mg/L Fe NPs showed an increase in TA concentration. Suanon et al. [75] observed that the TA content showed that methanogen bacteria were consuming VFAs, which led to an increase in CH_4 production [114].

The decomposition of organic materials by bacteria during anaerobic digestion leads to a decline in the solid. Either TS or VS removal is used to express it [115]. Three Fe NP doses (5, 10, and 20 mg/L) were examined by Abdelsalam et al. [71] to see how they affected the effectiveness of removing TS and VS from cattle manure. The greatest TS and VS removal performance was seen with 25 and 20%, respectively, at the conclusion of the experiment when the substrate was treated with 20 mg/L Fe NPs. In a similar manner, Farghali et al. [72] investigated the impact of adding Fe_2O_3 NPs on the effectiveness of removing TS and VS, and they found that the VS removal efficiency of 20 and 100 mg/L Fe_2O_3 NPs was 49.0% and 54.5%, respectively. On the TS removal efficiency, there isn't any information on a substantial difference. Additionally, a higher concentration of Fe NPs enhanced the clearance effectiveness of TS and VS. While Abdelsalam et al. [70] found that adding 20 mg/L of Fe_3O_4 NPs to the substrate (cattle manure) boosted the TS and VS removal effectiveness by 30% and 23%, respectively.

When the substrate (cattle manure) was treated with 500 mg/L Fe_3O_4 NPs, Farghali et al. observed that the TS and VS removal efficiency increased by 66 and 50.31%, respectively. The TS removal efficiencies of control, 15, 30, and 60 mg/L Fe NPs were 12.0%, 25.6%, 24.0%, and 20.7%, respectively [74]. These results are in agreement with those of Ali et al. [116], who showed that the TS removal effectiveness of the control (municipal solid waste-only), 50, 75, 100, and 125 mg/L Fe_3O_4 was 19.2%, 38.2%, 50.3%, 29.4%, and 27.4%, respectively. Additionally, for control, 15, 30, and 60 mg/L Fe NPs, the VS removal efficiency was 7.2%, 10.5%, 9.9%, and 9.6%, respectively. The VS removal effectiveness of control, 20, and 100 mg/L Fe_2O_3 was found to be 47.38%, 49.0%, and 54.5%, respectively. These results are in line with those of Farghali et al. [72], who also obtained similar results. Fe NPs improved the rate of decomposition of organic materials by enhancing the ability of methanogens bacteria to break down organic materials, as seen by changes in TS and VS levels with Fe NP usage.

2.3 Fertility evaluation of effluent containing iron nanoparticles

The availability of nitrogen (N), phosphorous (P), and potassium (K) in organic material was increased by microbial breakdown during digestion, enabling the effluent to be utilized as fertilizer alone or as a useful component of commercial fertilizers [117, 118]. NPK organic compound fertilizers have the potential to greatly enhance the physio-chemical properties of soil, enhancing the development of soil aggregate structure and raising the level of nutrient activation [119]. To determine the viability of using effluent containing Fe NPs as fertilizers, the effluent NPK content was assessed for various Fe NPs concentrations. With 15, 30, and 60 mg/L Fe NPs, the effluent NPK level was 5.84%, 5.70%, and 5.90%, respectively [120]. These effluents can be used as effective and promising organic fertilizer components since the NPK level of all Fe NPs effluents was close to the NPK content of bioorganic fertilizers.

3 Nickel nanoparticles

The bacteria use Ni as a track element throughout the anaerobic digestion process [121]. Ni is essential for the functioning of several hydrogenases, making it essential for both methanogenic and acidogenic bacteria [122]. CO dehydrogenase/acetyl-CoA synthase (Methanogens/Homoacetogens) and Methyl-CoM-reducates (Methanogens) are two instances of enzymes whose expression is influenced by Ni [55, 123, 124]. The cofactor F430, which is required for the methyl reductases complex to operate and catalyse the last stage of the CH_4 production process, also contains Ni [125].

3.1 Impacts of nickel nanoparticles on gas yield

Table 2 presents the effects of Ni NPs on the performance of the biogas production process and effluent quality under different process conditions. It is clearly seen that the effect Ni NPs is vary according to NPs concentration, size, process temperature, and substrate type.

Cattle manure was used in Abdelsalam et al. [58] investigation of the effect of Ni NPs on the production of biogas and CH_4 at a mesophilic temperature (37 °C). By achieving a 46.4–74.2% higher biogas production in anaerobic digestion and a 49.0–100% higher CH_4 yield compared to the control, they demonstrated that Ni NPs had a beneficial impact on cattle manure at the investigated concentration (0.5–2 mg/L). Furthermore, when the cattle manure was exposed to 0.5, 1, and 2 mg/L Ni NPs, respectively, the biogas production enhanced with the equivalent dosage of Ni NPs, reaching 486.7, 503.3, and 520 mL biogas on the first day. In the control experiment, which simply used cattle manure, the lag period lasted 11 days and produced just 416.7 mL of biogas. These results are in line with those of Abdelsalam et al. [70], who found that cattle manure exposed to 2 mg/L Ni NPs resulted in the highest biogas startup, producing 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 Fe_3O_4 NPs produced 596, 580, and 633.3 mL biogas,

The concentration of Ni NPs present, and the kind of substrate are important factors in the anaerobic digestion process [70, 71]. At three dosages of 3, 6, and 12 mg/L Ni NPs, Hassanein et al. [76] examined the effect of Ni NPs on CH_4 production from poultry litter. In comparison to the control experiment, the addition of 12 mg/L Ni NPs increased CH_4 production by 38.48%, resulting in 261 mL CH_4/g VS over the first 10 days as opposed to the same CH_4/g VS production over 69 days. In addition, within the first 29 days, 95.1% of the CH_4 produced by Ni NPs (12 mg/L) was produced. Similar results were found by Abdelwahab et al. [79], who found that adding 1, 2, and 4 mg/L of Ni NPs to cattle manure increased CH_4 production by 17.32%, 70.46%, and 53.79%, respectively, in comparison to using cattle manure only. He et al. [80] looked at how Ni NPs affected the production of CH_4 from sludge. Four different doses of Ni NPs were used: 1, 50, 200, and 600 mg/g-TSS (total suspended solids). The results showed that the CH_4 production was unaffected by the addition of 1 mg/g-TSS Ni NPs. As the dosage of Ni NPs was raised to 50 mg/g-TSS and above, there were adverse impacts on the CH_4 yield. The CH_4 yield was decreased by 89.3%, 84.33%, and 56.43%, respectively, when the substrates were treated with 50, 200, and 600 mg/g-TSS.

The bioavailability of methanogens was increased as a result of the majority of Ni potentially forming soluble organic complexes with specific amino acids [35]; additionally, Ni is a necessary component of the low molecular weight coenzyme F430, which uses two coenzymes-methyl thioether methyl coenzyme M and thiol coenzyme B-as substrates for the production of CH_4 in all methanogens [15, 126].

To examine the effect of Ni NPs on impurities like H_2S and CO_2 in the biogas, Hassanein et al. [76] studied the effect of three concentrations of Ni NPs (3, 6, and 12 Ni NPs) on the cumulative H_2S production of poultry litter. There was no discernible change in H_2S production between the substrate treated with 6 mg/L Ni NPs and the control condition (poultry litter only). The yield of H_2S was shown to be negatively impacted (10.7% increase) when the substrate was treated with 12 mg/L of Ni NPs. The production of H_2S improved when the substrate was exposed to 3 mg/L Ni NPs (5.9% decrease). In a different investigation, Abdelwahab et al. [79] showed that adding 2 mg/L Ni NPs to the cattle manure increased H_2S removal efficiency by 47.5%. Ni NPs had a 14.16% and a 34.16% removal efficiency at 1 and 4 mg/L, respectively.

These findings showed that all treated bio-digesters' H_2S production were successfully reduced by Ni NPs. The precipitation of metal sulfides, such as nickel sulfide (NiS) [78, 127, 128], may have reduced the amount of H_2S yield.

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

With a focus on the impact of Ni NPs on the stability of the anaerobic digestion process, Tsapekos et al. [78] investigated the effects of Ni NPs on pH, TA, and VFAs during the anaerobic digestion of sewage sludge at two concentrations (5 and 10 mg/Kg VS). To begin with, neither the pH nor the TA values of the treatment significantly deviated from those of the control. The author posits that the use of a significant amount of anaerobic inoculum may be the cause of the absence of significant changes [78].

Abdelwahab et al. [78], there are two phases to the pH shifts that occur at three concentrations of Ni NPs (1, 2, and 4 mg/L). The pH increased during the first stage, which lasted from the beginning of the experiment to day 20. Additionally, the greatest pH value of 7.3 was observed on Day 20 with 2 and 4 mg/L Ni NPs. The widespread usage of VFAs in anaerobic digestion systems, the oxidation of Ni to Ni+2, and an interaction between Ni and organic molecules in the medium are all possible causes of the pH rise. The substrate under anaerobic digestion will lose hydrogen ions (H+) as a result of the aforementioned reaction, raising the pH of the substrate. Additionally, CO_2 capture will prevent (H_2CO_3) from forming inside the substrate, which will raise the pH [88]. The pH drops throughout the second stage (from days 20 until shut down), mostly due to the accumulation of VFAs [114].

Additionally, the accumulation of VFAs showed a marked difference. VFAs in the form of acetate in (mg/L) were degraded by 1.39 and 1.38 times, respectively, when the substrates were treated with 5 and 10 mg Ni NPs/Kg VS and compared to an untreated substrate (control).

The effects of three different Ni NP concentrations (0.5, 1, and 2 mg/L) on the redaction of the TS and VS during the anaerobic digestion of cattle manure were investigated by Abdelsalam et al. [58]. The greatest TS and VS removal efficiency was achieved when the substrate was exposed to 2 mg/L Ni NPs, with final removal efficiencies of 33.3% and 26.3%, respectively. When the substrate (cattle manure) was treated with 2 mg/L Ni NPs, Abdelsalam et al. [70] found that the greatest TS and VS removal efficiency was achieved, with 28.0% and 20.4%, respectively. 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, but it was 23% and 20.4% for those two substances in VS. These results support those of Abdelwahab et al. [79] which reported that cattle manure alone, 1, 2, and 4 mg/L Ni NPs had TS removal efficiencies of 12.0%, 17.7%, 19.2%, and 16.2%, respectively. Additionally, for 1, 2, and 4 mg/L Ni NPs, the VS removal efficiencies were 7.2, 11.5, 12.1, and 10.6%, respectively.

3.3 Fertility evaluation of effluent containing nickel nanoparticles

For Ni NPs at 1, 2, and 4 mg/L, respectively, the digestates included 5.94%, 5.88%, and 5.86% NPK [79]. Bioorganic fertilizers should contain an NPK content of more than 5%, per the Indian Institute of Soil Science and the Indian Council of Agricultural Research. As a result, these digestates have excellent organic fertilizer components. Additionally, digestates had a greater TN (total nitrogen) than commercial bioorganic fertilizers and nutritional qualities that were equivalent to those of such fertilizers. The evidence points to the suitability of these digestates for soils with low nitrogen levels. Conversely, the TK (total potassium) content of these digestates was lower than that of commercial bio-organic fertilizer, a finding that was in line with the findings of fertility tests conducted on other cattle manure digestates [129, 130].

4 Cobalt nanoparticles

Cobalt has been shown to be an important trace mineral for the growth of methanogenic bacteria throughout the anaerobic digestion process [121]. Because cobalt is a protein cofactor of vitamin [131], it is necessary for methanogenic bacteria to break down methanol. Furthermore, it is considered that the use of Co is a key component in the oxidation of acetate to CO_2 and H_2, which leads to the hydrogenotrophic methanogenic process [55, 132].

4.1 Effects of cobalt nanoparticles on gas yield

Table 3 presents the effects of Co NPs on the performance of the biogas production process and effluent quality under different process conditions. It is clearly seen that the difference in the chemical composition of substrate and process condition makes the effect of Co NPs vary on biogas production.

Using a batch anaerobic digestion system, Abdelsalam et al. [70] investigated the effects of Co NPs (20 nm) on the production of biogas and CH_4 from cattle manure. When compared to the control, cumulative biogas production increased by 36.5 and 64.12%, respectively, when the substrate was treated with 0.5 and 1 mg/L Co NPs. These results are in line with those of Zaidi et al. [133], who found that adding Co NPs at a concentration of 1 mg/L during the anaerobic digestion of green microalgae increased biogas production by 9% in comparison to the control trial. The previously described decrease the amount of time needed to obtain maximal biogas and CH_4 production.

However, the addition of 2 mg/L Co NPs decreased the production of both biogas and CH_4 by 5.2 and 14.54%, respectively, in comparison to the control condition. Poultry litter with 1, 4, or 5.4 mg/L of Co NPs increased CH_4 production by 29, 26, and 30%, respectively [76]. Another research examined the effects of 1 mg/L Co NPs on anaerobic digestion using cattle manure as the substrate. In comparison to the control, biogas and CH_4 production have increased by 71.2 and 45.9%, respectively [70].

Abdelwhab et al. [81] found that the presence of 1 and 2 mg/L Co NPs enhanced cumulative biogas yield by 6.83% and 14.81%, respectively, when compared to control. When compared to cattle manure only, the cumulative biogas production did not significantly differ with 3 mg/L Co NPs. The addition of 1, 2, and 3 mg/L of Co NPs enhanced CH_4 production by 79.12%, 56.37%, and 54.65%, respectively, as compared to cattle manure alone. Additionally, when 2 mg/L and 3 mg/L of Co NPs were added to the substrate, no noticeable variations in CH_4 production were found. These results back up those made public by Zandvoort et al. [134], who found that the optimal dosage of Co is 0.8 mg/L. Additionally, the greatest CH_4 yield was attained when the substrate was exposed to 1 mg/L Co NPs, which is line with the observations of Abdelsalam et al. [70], who found that the presence of 1 mg/L Co NPs increased CH_4 production by 86% in comparison to the control condition (manure without NP additives). Additionally, the increase in CH_4 generated by 1 mg/L Co was in line with the results of Qiang et al. [135], Demirel and Scherer [130], and Feng et al. [136], all of whom reached the conclusion that Co is a crucial metal for methanogenesis because it functions as a metallic enzyme activator.

Hassanein et al. [76] investigation of the effects of Co NPs on H_2S production in biogas and anaerobic digestion process stability employed poultry litter in a mesophilic condition. They found that Co NPs have a beneficial effect on H_2S production in the tested concentration range (2.7–5.4 mg/L Co NPs), with H_2S production being 5.93–8.19% higher than in the control condition. However, when the substrate was treated with 1.4 mg/L Co NPs compared to the control setup, no significant variation in H_2S production was detected. When compared to cattle manure alone, cumulative H_2S production of 1, 2, and 3 mg/L Co NPs was shown to be reduced by 15.38%, 13.20%, and 57.89%, respectively Abdelwahab et al. [81] The greatest H_2S removal effectiveness of 57.89% was attained with the addition of 3 mg/L Co NPs. At 1 mg/L and 2 mg/L, Co NPs showed clearance efficiencies of 15.38 and 13.20%, respectively.

The formation of metal sulfide is one potential explanation for the reduction in H_2S production in this investigation [127, 128].

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

Focusing on VFA formation, TS and VS degradation throughout the fermentation process, Zaidi et al. [133] investigated the influence of 1 mg/L Co NPs on VFAs production during the anaerobic digestion of microalgal biomass after a 170 h fermentation period. The formation of VFA was significantly increased by the addition of 1 mg/L Co NPs.

Abdelsalam et al. [71] examined the impact of Co NPs in the concentration range of 0.5–2 mg/L on the efficiency of TS and VS removal in cattle manure. The maximum TS and VS removal efficiencies were achieved when the substrate was treated with 1 mg/L Co NPs, and they were 12.9% and 17.0%, respectively.

These results are in line with those of Abdelsalam et al. [70], who stated that the addition of 1 mg/L Co NPs increased the removal efficiency of TS and VS by 10.3% and 14.2%, respectively. As shown by the changes in TS and VS content following the addition of Co NPs, Co NPs accelerated the degradation of organic matter by increasing the ability of methanogens bacteria to break down organics. The TS removal effectiveness of cattle manure, 1, 2, and 3 mg/L Co NPs is determined to be 12.04%, 14.81%, 16.25%, and 14.81%, respectively, according to Abdelwhab et al. [81]. Additionally, 1, 2, and 3 mg/L Co NPs from cattle manure exhibit relative VS removal efficiencies of 11.55, 12.16, 11.85, and 10.66%.

4.3 Fertility evaluation of effluent containing cobalt nanoparticles

The total nitrogen, phosphorous, and potassium content of the digestate containing 1, 2, and 3 mg/L Co NPs is 5.32%, 4.68%, and 4.63%, respectively [81]. They can be used in combination with an artificial compound fertilizer since the total nutritional content of all Co NPs concentrations was close to 5%. In order to produce a high-quality organic compound fertilizer, the digestates were dewatered and dried. With NPK organic compound fertilizer, which promotes the formation of soil aggregate structure and raises the activation of soil nutrients, the physical and chemical characteristics of soil may be enhanced. It is clear that using NPK organic compound fertilizer reduces the amount of water that crops use, potentially resolving the region's ongoing water crisis issue. In order to produce an NPK organic compound fertilizer that enhances plant height, root length, root diameter, and dry weight, the anaerobic digestion digestate can be mixed with the three Co NPs [119].

5 Nanoparticle combinations

A recent development in the anaerobic digestion process is the combination of NPs to benefit from their distinctive features. This section of the review focuses on how a combination of NPs affects anaerobic digestion performance, particularly the level of H_2S in the resulting biogas and effluent quality.

5.1 Effects of nanoparticle combinations on gas yield

Table 4 presents the effects of nanoparticle combinations on the performance of the biogas production process and effluent quality under different process conditions. It is clearly seen that the combinations of nanoparticle can be used in different forms which makes the effect more attractive on the biogas production.

Iron, nickle, and cobalt NPs combinations have been shown to improve the start-up of biogas production by Abdelwahab et al. [69] In particular, the average biogas production of 30 mg/L Fe NPs + 2 mg/L Ni NPs + 1 mg/L

Co NPs, 30 mg/L Fe NPs + 2 mg/L Ni NPs, 30 mg/L Fe NPs + 1 mg/L Co NPs, and 2 mg/L Ni NPs + 1 mg/L Co NPs during the first five days of digestion was 41.82 mL/g VS (7.5% increase), 43.24 mL/g VS (12.67% increase), 42.18 mL/g VS (8.43% increase), and 40.0 mL/g VS (2.8% increase), compared to 38.90 mL/g VS.

Additionally, after 30 days, there was a significant increase in biogas yield (25.34%) when a combination of 30 mg/L Fe + 2 mg/L Ni + 1 mg/L Co NPs was used. There was also a significant increase in biogas yield (29.64%) when a combination of 30 mg/L Fe + 2 mg/L Ni NPs was used. Significant increase in biogas yield (19.68%) when a combination of 2 mg/L Ni + 1 mg/L Co NPs has been also achieved.

In a similar investigation, NP combinations of 500 mg/L nZVI + 4 g/L zeolite improve biogas production by 130.87% in compared to the control [82]. Similar results were obtained by Abdallah et al. [137], who found that utilising Ni-Ferrite NPs at concentrations of 20, 70, and 130 mg/L enhanced biogas production by 30.8%, 28.5%, and 17.9%, respectively, in comparison to using only cattle manure. Additionally, Karlsson et al. [138] reported that adding a combination of the chloride salts of Fe, Co, and Ni to a semi-continuous biogas reactor at concentrations of 500 Fe mg/L + 0.5 Co mg/L + 0.25 Ni mg/L, respectively, enhanced the biogas production by 23.91% in comparison to the control. According to Farghali et al. [72], the addition of NP combinations including 20 mg/L Fe_2O_3 NPs + 500 mg/L TiO_2 NPs and 100 mg/L Fe_2O_3 NPs + 500 mg/L TiO_2 NPs respectively increases biogas production by 10.07% and 13.08% when compared to control.

Additionally, Abdelwahab et al. [69]. found that the combination of 30 mg/L of Fe NPs + 2 mg/L of Ni NPs + 1 mg/L of Co NPs produced the highest daily CH_4 production (25.76 mL/g VS on day 10), whereas every other NP combination produced less CH_4 on a daily basis.

Morever, the cumulative CH_4 production of 30 mg/L Fe NPs + 2 mg/L Ni NPs + 1 mg/L Co NPs, 30 mg/L Fe NPs + 2 mg/L Ni NPs, 30 mg/L Fe NPs + 1 mg/L Co NPs, and 2 mg/L Ni NPs + 1 mg/L Co NPs were 329.37 mL/g VS (26.96%, increase), 318.78 mL/g VS (22.88, increase), 297.83 mL/g VS (14.81, increase), and 311.74 mL/g VS (20.17%, increase), respectively, while that of the cattle manure-only was (259.41 mL/g VS).

In a different research, Farghali et al. [72] found that the addition of NP combinations of 20 mg/L Fe_2O_3 NPs + 500 mg/L TiO_2 NPs and 100 mg/L Fe_2O_3 NPs + 500 mg/L TiO_2 NPs raised the cumulative CH_4 production from cattle manure by 13.32% (179.68 mL/g VS) and 14.96% (182.29 mL/g VS), respectively. Zitomer et al. [139] found that the presence of the salt mixture of Fe, Ni, and Co to propionate-substrate and acetate-substrate at a concentration of 25 mg/L each enhanced CH_4 production by 12 and 17%, respectively, in comparison to control.

Hassanein et al. [76] observed a negligible difference between poultry litter alone (305 mL/g VS) and a low NP combination (321 mL/g VS), which contained a combination of 400 mg/L of Fe NPs + 12 mg/L of Ni NPs + 5.4 mg/L of Co NPs. According to Abdelwahab et al. [69] the production of CH_4 may be efficiently increased by adding NP combinations. Furthermore, Fe, Ni, and Co NPs, which were able to combine the properties of each element to increase CH_4 yield, may be to responsible for the preference of the Fe/Ni/Co NP combinations over other NP combination additions and cattle manure alone. Namely, Fe oxidises to Fe2 + under anaerobic digestion, releasing two electrons. The hydrogenation pathway can be accelerated by the electrons released by Fe, increasing the production of CH_4 as inorganic CO_2 or acids consume them. Li et al. [93]. The methyl reductases complex, which catalyses the final stage of the CH_4 producing pathway, needs cofactor F430, a component of Ni, in order to function Thauer et al. [132]. While Co is a cofactor of carbon monoxide dehydrogenase and methyltransferases [140] (CODH). Both acetogenins and methanogens contain CODH, a crucial enzyme for the synthesis and consumption of acetate Zandvoort et al. [134].

In comparison to cattle manure alone, Abdelwahab et al. [69] found that NP combinations of 30 mg/L Fe NPs + 2 mg/L Ni NPs + 1 mg/L Co NPs, 30 mg/L Fe NPs + 2 mg/L Ni NPs, and 30 mg/L Fe NPs + 1 mg/L Co NPs considerably decreased cumulative H_2S production. Particularly, the total H_2S production was 794, 791, and 902 ppm correspondingly, compared to 926 ppm for the cattle manure only. However, compared to using only cattle manure, the cumulative H_2S production increased by 3.9% when the substrate was treated with NPs combinations of 2 mg/L Ni NPs + 1 mg/L Co NPs. In another study, Farghali et al. [72] found that the addition of NP combiations of 20 mg/L Fe_2O_3 NPs + 500 mg/L TiO_2 NPs and 100 mg/L Fe_2O_3 NPs + 500 mg/L TiO_2 NPs reduced the formation of H_2S by 163.66% and 117.13%, respectively, compared to the control. Similar to this, Hassanein et al. [76] found that adding NP combinations containing 1000 mg/L of Fe NPs + 120 mg/L of Ni NPs + 54 mg/L of Co NPs completely eliminated H_2S production. However, there was no discernible difference between the control and the lower concentration of NP combination, which contained 100 mg/L of Fe NPs + 12 mg/L of Ni NPs + 5.4 mg/L of Co NPs.

According to Abdelwahab et al. [69] all NP combinations showed evidence of H_2S redaction. Furthermore, the superiority of NP combinations containing Fe NPs, such as 30 mg/L Fe NPs + 2 mg/L Ni NPs + 1 mg/L Co NPs (28.72% increase), 30 mg/L Fe NPs + 2 mg/L Ni NPs

(28.90% increase), and Fe NPs + 1 mg/L Co NPs (14.47% increase), over NP combinations containing 2 mg/L Ni NPs + 1 mg (3.94% decrease). These findings suggested that a decrease in H_2S production may be caused by the Fe 2 + released from Fe combining with S2- during the anaerobic digestion process, which inhibits sulfate-reducing bacteria [50, 70, 72, 74, 76].

5.2 Effects of nanoparticle combinations on fundamental mechanisms of anaerobic digestion process

To start, pH values did not change from the cattle manure-only condition following exposure to all NP combinations [69]. Due to the large volume of anaerobic inoculum employed and the high buffer capacity of the biodigesters, there may not have been a discernible change. Tsapekos et al. [141]. According to Abdelwahab et al. [69] the VFAs degradation increased by 52.34%, 47.72%, 54.76%, 47.72 and 57.25% in the control, 30 mg/L Fe NPs + 2 mg/L Ni NPs + 1 mg/L Co NPs, 30 mg/L Fe NPs + 2 mg/L Ni NPs, 30 mg/L Fe NPs + 1 mg/L Co NPs. The TA improved by 11.90%, 9.52%, 14.28%, 20.23%, and 14.28% for the control, 30 mg/L Fe NPs + 2 mg/L Ni NPs + 1 mg/L Co NPs, 30 mg/L Fe NPs + 2 mg/L Ni NPs, 30 mg/L Fe NPs + 1 mg/L Co NPs, and 2 mg/L Ni NPs + 1 mg/L Co NPs, respectively. This suggested that NP combinations had a beneficial effect on digesting the VFAs as seen by the increase in TA of the substrate.

After a 30-day incubation period, Abdelwahab et al. [69] reported that the TS decrease was the same for all NP combinations of Fe, Ni, and Co. Along with the VS decrease in the control, the concentrations of 30 mg/L Fe NPs + 2 mg/L Ni NPs + 1 mg/L Co NPs, 30 mg/L Fe NPs + 2 mg/L Ni NPs, 30 mg/L Fe NPs + 1 mg/L Co NPs, and 2 mg/L Ni NPs + 1 mg/L Co NPs decreased by 10.95%, 16.11%, 15.14%, 19.62%. The changes in VS content caused by the addition of NP combinations showed that the NP combinations improved the ability of methanogenic bacteria to digest organics, which promoted the decomposition of the organic matter. These results were subordinate to those of Farghail et al. [72], who discovered that adding NP combinations of 20 mg/L Fe_2O_3 NPs + 500 mg/L TiO_2 NPs and 100 mg/L Fe_2O_3 NPs + 500 mg/L TiO_2 NPs increased the VS decomposition by 54.16% and 54.26%, respectively, in comparison to the control condition.

5.3 Fertility evaluation of effluent containing nanoparticle combinations

The nitrogen, phosphorous, and potassium concentrations of the digestates was 5.75%, 5.72%, and 5.95%, respectively, when the components Fe + Co, Fe + Ni and Fe + Co + Ni were combined. The Indian Institute of Soil Science recommends that bioorganic fertilizers have an NPK content that is more than 5%. As a consequence of this, the digestates in question are components of organic fertilizer that are both beneficial and potentially beneficial [142]. Abdelwahab et al. [120] found that the NPK content of the effluent was 5.20%, 5.36%, 5.16%, and 5.32 for 30 mg/L Fe NPs + 2 mg/L Ni NPs + 1 mg/L Co NPs, 30 mg/L Fe NPs + 2 mg/L Ni NPs, 30 mg/L Fe NPs + 1 mg/L Co NPs, and 2 mg/L Ni NPs + 1 mg/L Co NPs combinations, respectively. According to Indian Institute of Soil Science, bioorganic fertilizers should have an NPK concentration greater than 5%. As a result, these digestates are useful and promising organic fertilizer components.

6 Comparison of nanoparticles effects on average methane generation rate and effluent quality from anaerobic digestion of cattle manure

On the basis of the findings presented in above mentioned sections the most effective doses of NPs on average CH_4 production rate were explored and compared to others in Fig. 1. These dosages take the form of single NPs as well as its combinations. When compared to 30 mg/L of Fe NPs, 2 mg/L of Ni NPs, and 1 mg/L of Co NPs, respectively, the CH_4 production rate is increased by NP combinations of 30 mg/L of Fe + 2 mg/L of Ni + 1 mg/L of Co by 25.42%, 66.28%, and 59.29% [68, 69, 74, 79, 81, 120]. In order to explain these findings, it was determined that Fe, Ni, and Co NPs each performed a unique role in the promotion effects.

For particular, Fe NPs can function as an electron donor, release Fe 2+ into anaerobic systems, take part in the production of important enzymes, raise total hydrogen and methanogen consumption, change the modes of hydrolysis fermentation, and increase acetic acid content [75, 84, 85]. Because Ni is necessary for the operation of a large number of hydrogenases, it is required for acidogenic bacteria as well as methanogenic bacteria [122]). Specifically, Ni is involved in the development of enzymes such as CO dehydrogenase/acetyl-CoA synthase (Methanogens/Homoacetogens) and Methyl-CoM-reeducates (Methanogens). These enzymes are both required for the production of CH_4 [123, 124]. Ni is also found in the cofactor F430, which, according to Prakash et al. [125], is necessary for the proper functioning of the methyl reductases complex. This complex is responsible for catalysing the last step in the CH_4 production process [126, 132]. Additionally, Co is required (as a protein cofactor of vitamin) for the methanogenic bacteria to be able to break down methanol [131].

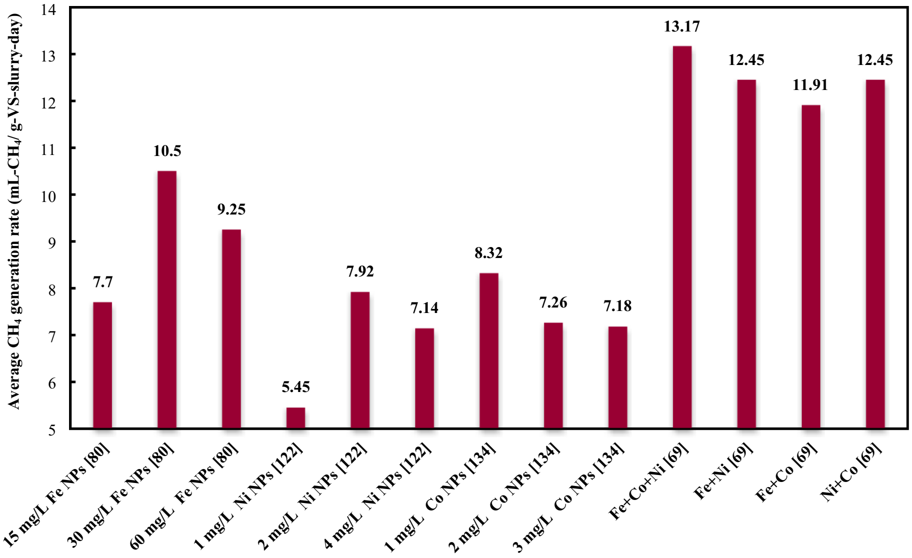

Fig. 1 Effect of different nanoparticle additives on average methane generation rate

In addition, the use of Co is regarded to be an essential component in the transformation of acetate into carbon dioxide and hydrogen gas, which ultimately results in the hydrogenotrophic methanogenic process [55, 132]. Take advantage of the one-of-a-kind characteristics that Fe, Ni, and Co NPs possess, which result in a greater CH_4 yield production rate. Based on these findings, it appeared as though the efficiency of a bio-digester to which Fe, Ni, and Co had been added may benefit from the use of a combination addition method.

Additionally, the most effective dosages of NPs on fertility evaluation of the effluent were investigated and compared to each other in Fig. 2. These dosages come in the form of single NPs as well as its combinations. In general, the utilization of various elements such as Fe, Ni, and Co at the same time led to an increase in the NPK content of the effluent [69, 142].

7 Challenges and future studies

The addition of various dosages of NPs promotes anaerobic bacteria and Archaea 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. In order to study the possibility of their reuse and decrease their environmental impact, Hassinen et al. [76, 143] studied various methods of tracking

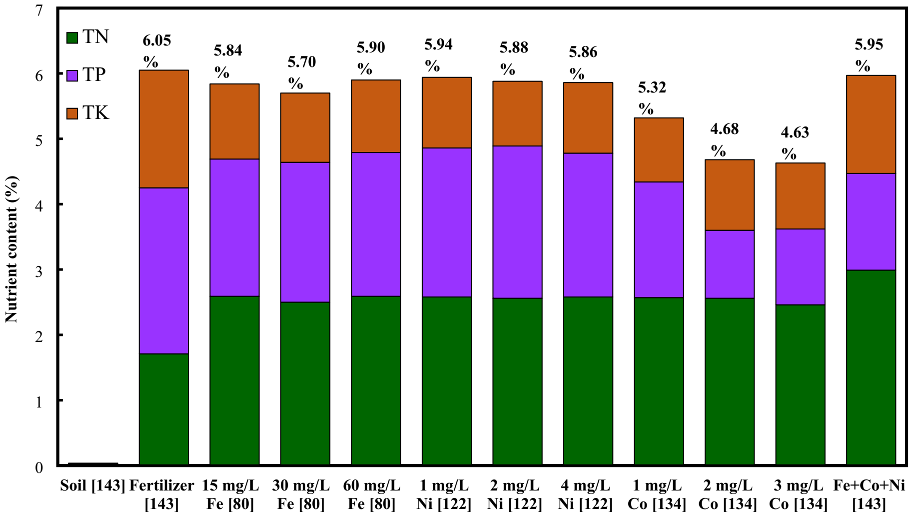

Fig. 2 The nitrogen, phosphorous, and potassium contents of soil, commercial bio-organic fertilizer and the effluent with different nanoparticle concentrations

nanoparticles inside the digester as well as the impact of using effluent that contains nanoparticles on the plant. However, their research did not sufficiently apply to the large size, so more study is required to address this issue.

8 Conclusions

The performance of anaerobic digestion with regard to gas production, process stability, and effluent quality can be affected by the addition of NPs to the anaerobic digestion of cattle manure in both positive and negative ways. Selected significant studies from several studies utilizing NP additives have been reviewed and presented in order to better understand recent activity in this field, according to a state-of-the-art literature review. The following findings can be taken from this review:

1. Single Fe, Ni, Co NPs is utilized in anaerobic digestion of cattle manure at concentration of 5–100 mg/L, 1–4 mg/L, and 1–3 mg/L to increase CH_4 production.
2. At concentrations more than 100 mg/L, Fe NPs can be used to reduce H_2S instead of enhancing CH_4 during the anaerobic digestion of cattle manure.
3. In the case of H_2S reduction, the use of single Ni and Co NPs in the anaerobic digestion of cattle manure is not recommended.
4. Among the single NPs, Ni NPs is preferred for stabilizing the anaerobic digestion process and improving the quality of the effluent.
5. The addition of NPs in the form of combination increased CH_4 production, further research is required to determine how it effects on the quality of effluent.
6. Nanoparticle combinations produce better results for improving CH_4 production when compared to adding NPs singly.

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Declarations

Conflict of interest 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.

Consent for publication All the authors approve this manuscript for publication.

Ethics approval and consent to participate All the authors abide by the ethics rules of the journal.

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