

Review

# Enhancement of Anaerobic Digestion with Nanomaterials: A Mini Review

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**Abstract:** In recent years, the number of articles reporting the addition of nanomaterials to enhance the process of anaerobic digestion has exponentially increased. The benefits of this addition can be observed from different aspects: an increase in biogas production, enrichment of methane in biogas, elimination of foaming problems, a more stable and robust operation, absence of inhibition problems, etc. In the literature, one of the current focuses of research on this topic is the mechanism responsible for this enhancement. In this sense, several hypotheses have been formulated, with the effect on the redox potential caused by nanoparticles probably being the most accepted, although supplementation with trace materials coming from nanomaterials and the changes in microbial populations have been also highlighted. The types of nanomaterials tested for the improvement of anaerobic digestion is today very diverse, although metallic and, especially, iron-based nanoparticles, are the most frequently used. In this paper, the abovementioned aspects are systematically reviewed. Another challenge that is treated is the lack of works reported in the continuous mode of operation, which hampers the commercial use of nanoparticles in full-scale anaerobic digesters.

**Keywords:** anaerobic digestion; nanomaterials; metallic nanoparticles; biogas; methane; operation mode



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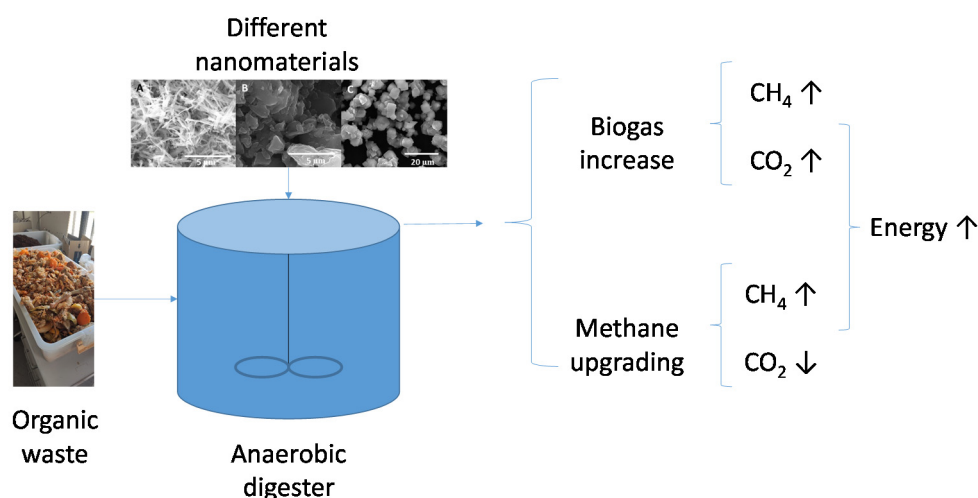
## 1. Introduction

Anaerobic digestion (AD) has become a worldwide strategy to obtain renewable energy from organic waste and by-products [1]. The principles of AD are well known, and this technology has been applied to a large number of organic wastes: food waste [2], sewage sludge [3], manure and slurry from farming facilities [4], etc. Briefly, a complex organic waste is composed of polymeric substances, such as proteins, fibers and fats, which are hydrolyzed into simple monomers, converted into volatile fatty acids and, finally, transformed into biogas, a gaseous mixture of methane (50 to 80%) and carbon dioxide (30 to 50%), with methane being produced in the last biological step involved in AD (i.e., methanogenesis) [5].

The first scientific papers where the positive effect of nanoparticles (NPs) on AD was discovered are relatively recent. Simultaneously, in 2014, two independent papers reported the enhancement of AD processes using magnetic iron oxide NPs [6,7]. Although preliminary, both studies demonstrated an increase in biogas production using two commonly anaerobically digested materials, such as sewage sludge, and other synthetic substrates in batch mode. The conclusions of both studies were relatively similar in terms of the higher production of biogas, and the reasons for such an increase were attributed to a better supplementation of iron and a consequent change in microbial populations, although the mechanism was not evident.

After these studies, numerous works dealing with AD and NPs have been reported. What are these beneficial effects of nanomaterials on anaerobic digestion? The general response is the increase in biogas, that is, methane production. However, this simple asseveration should be clarified, as it can be somehow confusing. For instance, it is well

known that other additives, such as biochar, increase the production of biogas [8]. However, the effect of nanomaterials can be detected on different parameters of the anaerobic digestion process. On the one hand, most studies published in the batch mode report significant increases in biogas production, which is the typical way to interpret this effect [9,10]. However, several recent studies carried out in the continuous mode reported a similar production of biogas, with this biogas being considerably enriched in methane content when some NPs were added [11,12]. In times of a worldwide energy crisis, this result is particularly interesting, as it supposes an in situ biogas upgrading (i.e., methane enrichment) that makes this renewable energy closer to the natural gas produced or obtained from fossil fuels. In fact, biogas upgrading is one emerging area of applied research for achieving ready-to-use methane, using several technologies that have severe economic restrictions [13,14]. Figure 1 explains these two different benefits.



**Figure 1.** Possible benefits involved in anaerobic digestion with nanoparticles.

Regarding economics, this is one of the main challenges of consolidating this strategy at the scientific level to make it possible at a commercial scale. This has not yet occurred, although some studies point to the price of NPs as the main aspect to consider for a competitive process, as expected [15].

The main objective of this review was to update the most recent information regarding the benefits of the use of nanomaterials in AD. Critical points are especially addressed: (i) the nanomaterials used in AD enhancement (both metallic NPs and other nanomaterials); (ii) the mechanisms proposed for such AD enhancement, especially changes in the redox potential and in microbial populations; (iii) the mode of operation studied, highlighting the need for continuous pilot reactor studies to implement this strategy at the commercial level. Other important aspects such as the presence of nanomaterials in digestate or their possible recovery and reuse were not treated in this review.

## 2. Nanomaterials Used in Anaerobic Digestion

Not intended as a full review, Tables 1 and 2 show several representative examples of recently published papers in which nanomaterials improved some aspect of AD, especially an increase in biogas or methane. These tables do not aim to be a complete compilation of works recently published on this topic, as the list would be impossible to present in a single paper (a simple search of the Scopus<sup>®</sup> database for the terms “anaerobic digestion” and “nanomaterials” or “nanoparticles” reports more than 600 papers).

**Table 1.** Examples of studies using inorganic metallic nanoparticles and their effect on anaerobic digestion.

Nanoparticle	Effect Observed	Operation Mode and Particularities	Reference
Cu and Fe oxides	Biogas and methane increase	Batch, iron and copper NPs were synthesized by hydrothermal treatment of corn straw	[16]
Co ferrate	Biogas and methane increase	Batch, NP addition enhanced H <sub>2</sub> /CO <sub>2</sub> methanogenesis pathway. Excess NPs revealed negative effects	[17]
Cu and Fe oxides	Biogas and methane increase	Batch, review of microbial mechanisms	[18]
Fe zero-valent	Biogas increase and methane enrichment	Continuous, increase in the biodegradability of fibers due to the presence of NPs	[19]
Zn oxide	Biogas and methane increase	Batch, inhibition observed at high ZnO NPs concentrations	[20]
Fe zero-valent	Methane enrichment	Continuous, increase in the methane content of biogas, under both thermophilic and mesophilic conditions	[12]
Ti and Fe oxides	Biogas and methane increase	Semicontinuous, NPs and salts boosted methane production for lignocellulosic materials	[21]
Fe zero-valent	Methane enrichment	Semicontinuous, the increase in the oxidation state of NPs seemed to be related to the loss of effect over time	[11]
Ti oxide	Biogas increase and fast hydrolysis and acidogenesis	Batch, hydrolysis and acidogenesis rates have been enhanced due to the addition of NPs	[22]
Fe oxide	Biogas increase and inhibition of H <sub>2</sub> S production	Batch, high rate of H <sub>2</sub> S production decrease (from 50 to 80%)	[23]
Fe zero-valent	Methane increase and better stability	Batch, NPs promoted the acidogenesis–acetogenesis without acidification	[24]

**Table 2.** Examples of studies using other nanomaterials and their effect on anaerobic digestion.

Nanoparticle	Effect Observed	Operation Mode	Reference
Graphene oxide	Biogas and methane increase	Batch, cumulative methane yield was highly dependent on the dosage	[25]
Nano-biochar	Biogas and methane increase	Batch, review focused mainly on biochar	[26]
Graphene	Biogas and methane increase	Batch, low temperature did not affect archaeal community compositions with graphene and methane increase	[27]
Carbon nanotubes	Biogas and methane increase; mitigation of ammonia inhibition	Batch, carbon nanotubes may mitigate or worsen the ammonia inhibition depending on the total ammonia nitrogen	[28]
Graphite, graphene and graphene oxide	Biogas and methane increase	Batch, graphene exhibited the best performance by removing some antibiotic resistance genes	[29]
Graphene	Biogas and methane increase	Batch, direct interspecies electron transfer (DIET) via graphene was established	[30]

The distribution of the tables was performed according to the materials used: Table 1 compiles the works that used inorganic metallic NPs, whereas Table 2 shows the works carried out with other nanomaterials.

As observed in Tables 1 and 2, as well as in most of the references consulted, several conclusions can be stated regarding the use of different types of nanomaterials in anaerobic digestion:

- (a) Among all the nanomaterials used, inorganic metallic NPs were, by far, the most used to enhance the process of anaerobic digestion. In the case of C-based NPs, practically all the works used graphene or graphene oxide;
- (b) Among all the inorganic metallic NPs used, those based on iron, zero-valent and oxide forms were the most frequently used, with specific reviews on this point [31,32];
- (c) There existed a significant number of studies related to the use of a combination of metallic NPs, reporting better results than that of a single type of NP (Table 1). Obviously, this needs a careful economic assessment, which was not often presented;
- (d) A few number of works used metallic NPs covered with a kind of coating, with the main objective being preventing the oxidation of the NPs [33,34];
- (e) Another very small number of publications reported a negative effect of NPs on the process of anaerobic digestion [35,36]. Usually, the inhibition provoked by NPs was only observed at high dosages;
- (f) There is a concerning lack of information regarding the characteristics of digested materials (both liquid fraction and solid fraction after dehydration). It is clear that

some NPs can be negative for a material that is supposed to be applied to soil as an organic amendment.

Of course, these conclusions, within a research field clearly in expansion, can change over the following years [31].

### 3. Mechanisms of Enhancement

The different mechanisms that have been hypothesized or experimentally tested regarding the positive effect of the addition of nanomaterials to anaerobic digestion have changed over the last years, according to new knowledge achieved. For instance, the first works [6,7] explained the increase in biogas by a controlled release of iron from the dilution of NPs for microorganisms and by the presence of syntrophic communities involved in electron transfer, respectively. However, it must be taken into account that these were preliminary studies conducted under batch conditions, where some effects, such as population dynamics, are difficult to discuss.

Recent works, especially those performed at continuous or semicontinuous operation, have gained knowledge regarding the anaerobic microbial communities that are predominant when NPs are added to the media. In summary, the most confirmed hypothesis points out that modifications of the microbial populations are correlated to the increased biogas production [37]. Specifically, the enhancement of methane production by *Methanosarcina barkeri* using magnetite NPs was reported that [11,38,39]. More generally, Bacteria *Syntrophomonas* and Archaea *Methanosarcina* are the dominating enriched syntrophic partners, and the expression of functional genes involved in carbon dioxide reduction to the methane pathway is increased. Therefore, a more efficient fermentative hydrogen and methane coproduction system by improving microbial electron transfer was observed with the presence of iron-based NPs [40].

It is also hypothesized that the state of oxidation of iron NPs is a key parameter for biogas or methane increase. Some studies dealing with wastewater sludge [11] and pig manure [12], studied in detail in the oxidation state, highlighted the iron state of oxidation as a promoter for increasing methane in anaerobic digestion. A schematic drawing of the mechanisms of enhancement is presented in Figure 2.

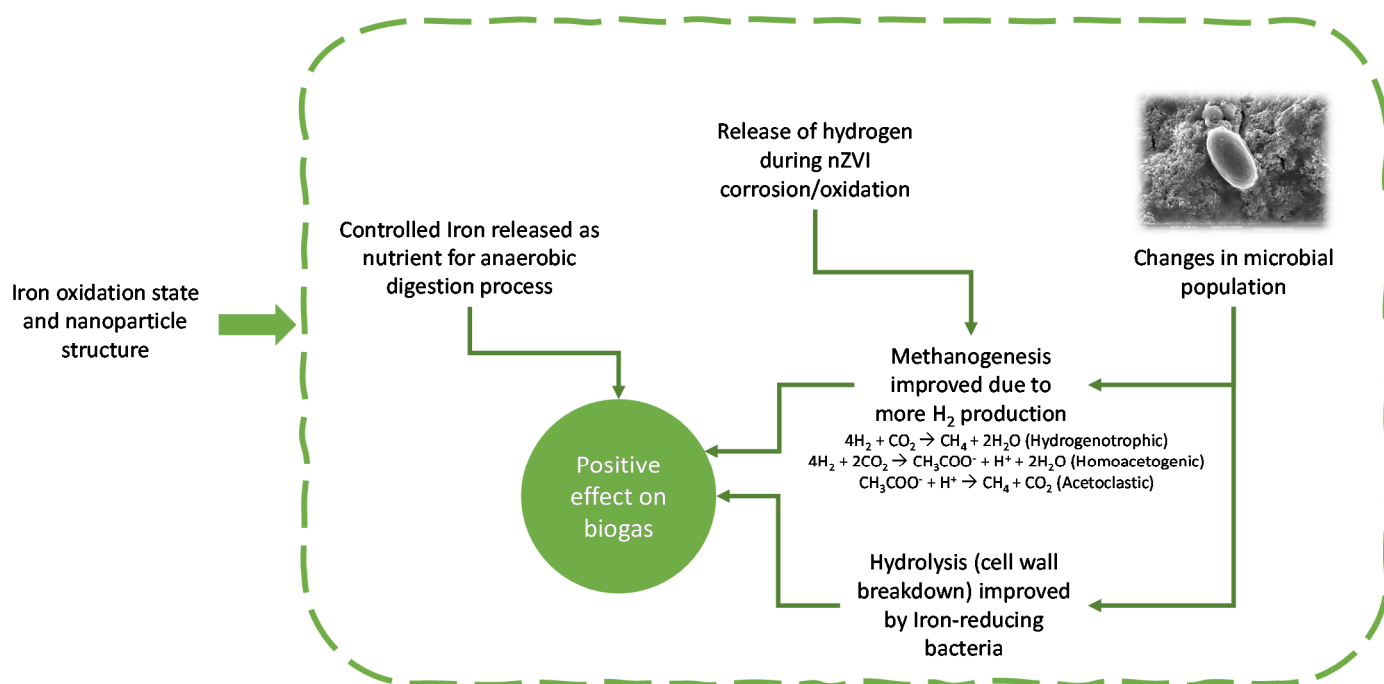


Figure 2. Scheme of the mechanisms proposed by the enhancement of anaerobic digestion using nanomaterials.

It must be kept in mind that all these works were conducted with iron-based (i.e., zero-valent or oxide) NPs. To our knowledge, only one work with the combined addition of iron and titanium oxide NPs in the anaerobic digestion of manure from dairy cattle is available in the literature [21]. In this study, iron NPs present a positive effect, with a 60% increase in methane, whereas titanium oxide NPs were inhibitory.

However, the reader should consider that the number of conditions, concentrations of NPs, and modes of operation (i.e., continuous, semicontinuous or batch) is very large, which makes it difficult to interpret and compare results from different studies [31].

## 4. Results According to the Operation Mode

### 4.1. Batch Mode

As observed in Tables 1 and 2 and reviewing the recent literature, most of the results obtained at this moment of research were still carried out under batch mode conditions. This implies that some results could not be completely reproducible in the semicontinuous or full continuous mode, which are the ways full-scale digesters work. However, some authors point out that batch experiments, conducted as typical biochemical methane potential (BMP) tests, can be a first approach to the effects of some additives or in anaerobic co-digestion assays [41], especially to obtain kinetic data and methane production. Other papers related to the scale-up effects point to several negative effects when comparing batch results and those obtained at higher scales, derived from difficulties in mixing and homogenization, which result in lower methane yields as well as the net electricity produced (20–30% decrease) [42]. Thus, it is evident that batch tests present several limitations. In addition to the above, acclimation to inhibition cannot be determined, a well-known effect observed in the continuous mode for a wide variety of inhibitors (ammonia, volatile fatty acids, long-chain fatty acids, metals, etc.). In addition, it is evident that batch tests can only simulate mixed reactors [43] but not more complex anaerobic reactors [44]. This is the reason why most recent anaerobic digestion studies in which methane yields are used to reproduce full-scale reactors are performed in a continuous mode of operation [12,45,46]. Other possibilities of operation (for instance, semi-batch or fed-batch) are rarely used in pilot of full-scale anaerobic digesters. To our knowledge, no literature has been found on the use of nanomaterials using these operational strategies.

### 4.2. Continuous Operation

For the reasons explained in the previous point, this mini-review focused on recent continuous (often semicontinuous) studies on the effect of nanomaterials in anaerobic digestion. This can be considered an emerging trend in this topic, and it is obviously the previous step to promote full-scale anaerobic digestion operations with NPs. In this case, the number of studies published is small. Moreover, in some cases, the reader must be careful, as some papers are not strictly related to nanomaterials as they are defined: sizes between approximately 1 and 100 nanometers [47]. In this case, they must be considered as additives, which is a more conventional topic studied in anaerobic digestion [48].

According to the studies published, the continuous anaerobic digestion process at the pilot scale is often performed under semicontinuous operation, that is, intermittent feeding. Regarding NP feeding, several methods have been reported. For instance, Cerrillo et al. (2021) used a classical semicontinuous method with weekly additions of a zero-valent iron NP pulse in the mesophilic and thermophilic anaerobic digestion of pig slurry [12]. The authors reported an increase in the content of methane in the biogas in the thermophilic reactor from 64% to a maximum value of 87%. Approximately, the same values were obtained in the mesophilic reactor. The authors justified this increase by the highest specific methanogenic activity detected with NPs. One important observation from this paper is that batch experiments at mesophilic temperature showed an inhibition of methane production at all tested NP dosages (i.e., 42, 84, 168 and 254 mg g<sup>-1</sup> VSS concentrations), while methane production was boosted with the lowest dosage in thermophilic conditions. This highlights an important fact that has been observed in other works: the results of batch experiments

cannot be directly extrapolated to continuous experiments, given the typical phenomenon of the acclimation of anaerobic microorganisms to inhibition conditions [12]. In another work treating wastewater sludge (a mixture of primary and secondary sludge), Barrena et al. (2021) tested the sustained effect of zero-valent iron NPs in the process of anaerobic digestion [11]. The authors observed some interesting effects. Similar to [12], punctual doses every 5–7 days sustained positive effects with higher methane content. However, NP oxidation was observed by TEM-EELS (transmission electron microscope-electron energy-loss spectroscopy) analysis, which implies the loss of the effect on methane increase over time. The authors proposed a strategy based on using the magnetic retention of NPs to partially overcome this problem and to reduce the use of NPs, with positive results. When retaining or reusing NPs, it is very important to understand the role of the oxidation state on the enhancement of the anaerobic digestion process. These abovementioned studies [11,12] are of special interest, since they studied the microbial consortium with a marked increase in the relative abundance of members assigned to the *Methanothrix* genus, recognized as an acetoclastic species showing high affinity for acetate, which explains the rise of methane content in the biogas (Figure 1). Other recent works support these findings. For example, Juntupally et al. (2022), when adding iron oxide NPs into the anaerobic digestion of food waste at mesophilic and thermophilic temperatures, observed that the methane content increased from 60% to 74% at 35 °C and 62 to 78% at 55 °C at a dose of 4 g/L of NPs [49]. Again, a syntrophic balance between the bacterial groups (i.e., *Firmicutes*, *Bacteroidetes*, *Chloroflexi* and *Thermotogae*) and archaeal groups (i.e., *Methanosarcina*, *Methanothrix* and *Methanosaeta*) was observed. Moreover, Dong et al. (2022) also observed that based on a detailed microbial community analysis, biomethanation by using zero-valent iron and zero-valent iron NPs depended on hydrogenotrophic methanogenesis in the anaerobic biomethanation of carbon dioxide [50].

Other works focused on the changes in metabolism when using iron-based NPs. For instance, Zang et al. (2020) attributed the increase in methane production to the consumption of extracellular polymeric substances (EPS) when using iron oxide NPs in the anaerobic digestion of waste sludge that resulted in a considerable decrease in organic matter [51].

Recently, research has been published on the use of NPs to enhance anaerobic digestion. These novel papers also observed an increase in methane production, but in addition, they found specific phenomena that are worthy of comment, especially as they were studied in semicontinuous processes, that is, close to realistic AD conditions. One point that was recently observed is the use of genetics. On the one hand, several authors have used genetic studies (16S rRNA gene sequencing) to confirm that the percentage of hydrogen-utilizing methanogens (*Methanolinea*) was up to 62.6% of total archaeal sequences when using magnetite NPs [52]. On the other hand, other authors have used genetic techniques to conclude that macrolide, aminoglycoside, and beta-lactam resistance genes are less abundant in the presence of magnetite NPs, which is a new relevant point, as it confirms that the presence of NPs in AD processes is beneficial for the removal of some antibiotic-resistant genes [53]. Another clear field of research is the use of advanced configurations of bioreactors commonly used in AD processes with the addition of NPs. This is the case for UASB (upflow anaerobic sludge blanket) reactors, where zinc oxide nanoparticles immobilized by methylenebisacrylamide were used [54]. In this case, biomass retention capacity was observed to improve carbon dioxide sequestration and to increase methane production using oil palm wastewater. Another later paper on granular sludge reported a magnetite nanoparticles-modified *Aspergillus tubingensis* mycelium pellet-based anaerobic granular sludge for AD food waste treatment. In this case, NPs stimulated extracellular polymeric substances (EPS), which protected the microbes from high osmotic pressure, resulting in higher methane yields than activated flocculent sludge [55]. Other papers go a step further and report the presence of magnetite NPs in digestate when used as fertilizer for lettuce crops, which also presented a higher presence of NPs in lettuce biomass (21.0–1,920%). This study showed that the effects of the NPs remaining in the AD effluent

must be considered in future works, an issue that is not treated in the scientific literature [56]. Probably, as this research is at an emerging point with new publications appearing each week, new effects of NPs on AD processes will be discovered and become a topic of novel research studies, especially in the use of advanced microbiological techniques and in the development of new AD reactor configurations.

As expected, most of these continuous works were carried out using iron-based NPs, except from a study with silver NPs [57], with the objective to determine the toxicity of this biocide material, which was not observed (even methane production was enhanced), and a study related to the recovery of tellurium NPs by the continuous reduction of tellurite using an UASB reactor [58]. It is evident that the small number of studies related to semicontinuous processes were focused on technical issues, and it is expected that in the short-term future, other aspects will be studied.

#### 4.3. Dosage and Dosing Strategy

Dosage is an important issue in all environmental applications of nanomaterials. In fact, one crucial particularity of these materials is a very high surface/volume ratio, in comparison with non-nanomaterials, which provide enhanced properties in terms of adsorption, catalytic activity, etc. [6]. In consequence, it is expected that the number of nanoparticles to enhance anaerobic digestion is lower than those of other typical additives used in this technology. Thus, it is reported that a significant amount of biochar can retrieve 89% of the ultimate biomethane potential [59], although other authors point out that the cost of biochar does not compensate for the extra production of methane [8]. A similar situation occurs when using iron for biogas desulfuration, where stoichiometric dosages must be used, although biochar can also have a significant role [60]. In the case of nanoparticles, stoichiometry is not relevant and, consequently, dosages are lower [11,12].

Nevertheless, and considering that the normal mode of operation in full-scale anaerobic digesters is a continuous or semicontinuous substrate feeding, there is some uncertainty on how to feed nanomaterials. In this case, only pilot-scale systems are available in the literature, and the typical strategy is a semicontinuous dosing of NPs, which can be coupled with the substrate addition, although uncoupling between the substrate and NP addition has also been reported (for instance, substrate on a daily basis and NPs every two or three days, or even weekly) [11,12]. It is evident that with the proliferation of continuous studies, the strategy of nanomaterial feeding will play a key role in the enhancement of methane production.

These two critical points are also very important in the life cycle assessment of the overall strategy when using a product such as nanomaterials for the improvement of processes such as anaerobic digestion, which is a technology for obtaining renewable energy. It is clear that a complete sustainability analysis (from environmental and economic perspectives) is necessary. Unfortunately, only very recently have some general reports regarding the sustainable design of engineered nanomaterials and the future prospects of the life cycle assessment of nanomaterials been published [61,62].

## 5. Future Challenges

Obviously, the main future challenge for the massive implementation of the use of NPs in full-scale anaerobic digesters is their cost. The fact that most studies are carried out in a lab or, in the best cases, at the pilot scale, does not help this implementation. In the case of batch studies, these are even more limited, as the conditions are not realistic when compared to those of continuous or semicontinuous full-scale digesters. In consequence, the main drawback is the cost of NPs. This can be partially overcome by two combined strategies that are interesting to explore:

1. The use of low-cost iron-based NPs, which could easily be available around the entire world and, sometimes, can be obtained from waste. In this case, it is mandatory to use easily scalable synthesis methods. Xu et al. (2022) presented a complete review regarding methods for producing iron NPs, including their environmental impact.

From this work, it is evident that some of these methods could be easily implemented at a commercial scale [63];

2. Another important point for decreasing the cost of nanomaterials is the reuse of NPs in several cycles of anaerobic digestion. Although this has been tested in other related fields, such as the recovery of microalgae in wastewater treatment [64], no evidence exists for anaerobic digestion with NPs, although some results have been published with 100–700 nm magnetite [47], except from that related to semicontinuous processes, where NPs are retained in the digester and continuous addition of NPs is not necessary [11].

Another future challenge that is not properly addressed in the current research is the characterization and possible uses of digestate. As iron is a nontoxic metal, this is another point that favors the use of iron-based NPs, although the information is practically nonexistent. For instance, a study by Suanon et al. (2016), using zero-valent iron and magnetite NPs, commented that iron NPs promoted the immobilization of phosphorus in the solid digestate, which is a very positive effect [65].

Finally, for an easier comparison among studies, it would be important to report the results in the same units. Thus, it is proposed to report the NP dose values as NP mass per VS of substrate added to the reactor, and the biogas or methane production as a volume of gas per mass of VS added, and the volume of gas in normal conditions per volume of the reactor.

## 6. Conclusions

Finally, some conclusions can be extracted from this mini-review:

- The use of nanomaterials to enhance anaerobic digestion is an emerging trend of research, with a large body of evidence at the lab and pilot scales;
- Unfortunately, there are no studies at the full-scale and few at the pilot scale, which hinders the commercialization of nanomaterials as an enhancer for anaerobic digestion;
- Among the nanomaterials tested, iron-based NPs appear to be the most promising in terms of biogas and methane increase and, as an extra factor, the possibility of being magnetically separated and reused;
- Mechanisms of enhancement are still under study, but the influence of NPs on the state of oxidation and redox potential in the mixture seems to be the most accepted.

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## References

1. Lora Granado, R.; Souza Antune, A.D.; Valéria da Fonseca, F.; Sánchez, A.; Barrena, R.; Font, X. Technology Overview of Biogas production in anaerobic digestion plants: A European Evaluation of Research and Development. *Renew. Sust. Energ. Rev.* **2017**, *80*, 44–53. [[CrossRef](#)]
2. Komilis, D.; Barrena, R.; Lora Grando, R.; Vogiatzi, V.; Sánchez, A.; Font, X. A state of the art literature review on anaerobic digestion of food waste: Influential operating parameters on methane yield. *Rev. Environ. Sci. Biotechnol.* **2017**, *16*, 347–360. [[CrossRef](#)]



3. Tauber, J.; Ramsbacher, A.; Svardal, K.; Krampe, J. Energetic Potential for Biological Methanation in Anaerobic Sewage Sludge Digesters in Austria. *Energies* **2021**, *14*, 6618. [[CrossRef](#)]
4. O'Connor, S.; Ehimen, E.; Pillai, S.C.; Lyons, G.; Bartlett, J. Economic and Environmental Analysis of Small-Scale Anaerobic Digestion Plants on Irish Dairy Farms. *Energies* **2020**, *13*, 637. [[CrossRef](#)]
5. Tonanzi, B.; Crognale, S.; Gianico, A.; Della Sala, S.; Miana, P.; Zaccone, M.C.; Rossetti, S. Microbial Community Successional Changes in a Full-Scale Mesophilic Anaerobic Digester from the Start-Up to the Steady-State Conditions. *Microorganisms* **2021**, *9*, 2581. [[CrossRef](#)]
6. Casals, E.; Barrena, R.; García, A.; González, E.; Delgado, L.; Busquets-Fité, M.; Font, X.; Arbiol, J.; Glatzel, P.; Kvashnina, K.; et al. Programmed iron oxide nanoparticles disintegration in anaerobic digesters boosts biogas production. *Small* **2014**, *10*, 2801–2808. [[CrossRef](#)]
7. Cruz Viggì, C.; Rossetti, S.; Fazi, S.; Paiano, P.; Majone, M.; Aulenta, F. Magnetite particles triggering a faster and more robust syntrophic pathway of methanogenic propionate degradation. *Environ. Sci. Technol.* **2014**, *48*, 7536–7543. [[CrossRef](#)]
8. González-Arias, J.; Martínez, E.J.; Gómez, X.; Sánchez, M.E.; Cara-Jiménez, J. Enhancing biomethane production by biochar addition during anaerobic digestion is economically unprofitable. *Environ. Chem. Lett.* **2022**, *20*, 991–997. [[CrossRef](#)]
9. Kweinor-Tetteh, E.; Rathilal, S. Kinetics and Nanoparticle Catalytic Enhancement of Biogas Production from Wastewater Using a Magnetized Biochemical Methane Potential (MBMP) System. *Catalysts* **2020**, *10*, 1200. [[CrossRef](#)]
10. Abdelsalam, E.; Samer, M.; Attia, Y.A.; Abdel-Hadi, M.A.; Hassan, H.A.; Badr, Y. Influence of zero valent iron nanoparticles and magnetic iron oxide nanoparticles on biogas and methane production from anaerobic digestion of manure. *Energy* **2017**, *120*, 842–853. [[CrossRef](#)]
11. Barrena, R.; Vargas-García, M.C.; Capella, G.; Barańska, M.; Puentes, V.; Moral-Vico, J.; Sánchez, A.; Font, X. Sustained effect of zero-valent iron nanoparticles under semi-continuous anaerobic digestion of sewage sludge: Evolution of nanoparticles and microbial community dynamics. *Sci. Total Environ.* **2021**, *777*, 145969. [[CrossRef](#)] [[PubMed](#)]
12. Cerrillo, M.; Burgos, L.; Ruiz, B.; Barrena, R.; Moral-Vico, J.; Font, X.; Sánchez, A.; Bonmatí, A. In-situ methane enrichment in continuous anaerobic digestion of pig slurry by zero-valent iron nanoparticles addition under mesophilic and thermophilic conditions. *Renew. Energy* **2021**, *180*, 372–382. [[CrossRef](#)]
13. Kweinor-Tetteh, E.; Rathilal, S. Biophotocatalytic Reduction of CO<sub>2</sub> in Anaerobic Biogas Produced from Wastewater Treatment Using an Integrated System. *Catalysts* **2022**, *12*, 76. [[CrossRef](#)]
14. Lawson, N.; Alvarado-Morales, M.; Tsapekos, P.; Angelidaki, I. Techno-Economic Assessment of Biological Biogas Upgrading Based on Danish Biogas Plants. *Energies* **2021**, *14*, 8252. [[CrossRef](#)]
15. Hassaan, M.A.; Pantaleo, A.; Santoro, F.; Elkatory, M.R.; De Mastro, G.; El Sikaily, A.; Ragab, S.; El Nemr, A. Techno-Economic Analysis of ZnO Nanoparticles Pretreatments for Biogas Production from Barley Straw. *Energies* **2020**, *13*, 5001. [[CrossRef](#)]
16. Dong, Z.; Guo, H.; Zhang, M.; Xia, D.; Yin, X.; Lv, J. Enhancing biomethane yield of coal in anaerobic digestion using iron/copper nanoparticles synthesized from corn straw extract. *Fuel* **2022**, *319*, 123664. [[CrossRef](#)]
17. Zhang, H.; Li, W.; Zhou, C.; Zhang, J.; Pei, Y.; Zang, L. Comparison of cobalt ferrate-based nanoparticles for promoting biomethane evolution from lactic acid anaerobic digestion. *Bioresour. Technol.* **2022**, *347*, 126689. [[CrossRef](#)]
18. Jadhav, P.; Khalid, Z.B.; Zularisam, A.W.; Krishnan, S.; Nasrullah, M.; Nasrullah, M. The role of iron-based nanoparticles (Fe-NPs) on methanogenesis in anaerobic digestion (AD) performance. *Environ. Res.* **2022**, *204*, 112043. [[CrossRef](#)]
19. Gundoshmian, T.M.; Ahmadi-Pirlou, M. Increasing biogas and methane yield by adding sewage sludge and zero-valent iron nanoparticles during the single-stage anaerobic digestion with municipal solid waste. *Int. J. Energy Res.* **2022**, *46*, 1–13. [[CrossRef](#)]
20. Qi, L.; Liu, X.; Miao, Y.; Chatzisympson, E.; Yang, P.; Lu, H.; Pang, L. Response of cattle manure anaerobic digestion to zinc oxide nanoparticles: Methane production, microbial community, and functions. *J. Environ. Chem. Eng.* **2021**, *9*, 106704. [[CrossRef](#)]
21. Farghali, M.; Ahmed, M.M.; Kotb, S.; Iwasaki, M.; Ihara, I.; Umetsu, K. Steady state of semi-continuous anaerobic digestion of cattle manure under the stress of adding iron and titanium oxide nanoparticles. *J. Mater. Cycles Waste Manag.* **2021**, *23*, 1930–1937. [[CrossRef](#)]
22. Ghofrani-Isfahani, P.; Baniamerian, H.; Tsapekos, P.; Alvarado-Morales, M.; Kasama, T.; Shahrokhi, M. Effect of metal oxide based TiO<sub>2</sub> nanoparticles on anaerobic digestion process of lignocellulosic substrate. *Energy* **2020**, *19115*, 116580. [[CrossRef](#)]
23. Farghali, M.; Andriamanohiarisoamanana, F.J.; Ahmed, M.M.; Kotb, S.; Yamamoto, Y.; Iwasaki, M.; Yamashiro, T.; Umetsu, K. Prospects for biogas production and H<sub>2</sub>S control from the anaerobic digestion of cattle manure: The influence of microscale waste iron powder and iron oxide nanoparticles. *Waste Manag.* **2020**, *101*, 141–1491. [[CrossRef](#)] [[PubMed](#)]
24. Lizama, A.C.; Figueiras, C.C.; Pedreguera, A.Z.; Ruiz Espinoza, J.E. Enhancing the performance and stability of the anaerobic digestion of sewage sludge by zero valent iron nanoparticles dosage. *Bioresour. Technol.* **2019**, *275*, 352–359. [[CrossRef](#)] [[PubMed](#)]
25. Kaushal, R.; Baitha, R. Biogas and methane yield enhancement using graphene oxide nanoparticles and Ca(OH)<sub>2</sub> pre-treatment in anaerobic digestion. *Int. J. Ambient Energy* **2021**, *42*, 618–625. [[CrossRef](#)]
26. Goswami, L.; Kushwaha, A.; Singh, A.; Saha, P.; Choi, Y.; Maharana, M.; Patil, S.V.; Kim, B.S. Nano-Biochar as a Sustainable Catalyst for Anaerobic Digestion: A Synergetic Closed-Loop Approach. *Catalysts* **2022**, *12*, 186. [[CrossRef](#)]
27. Tian, T.; Qiao, S.; Li, X.; Zhang, M.; Zhou, J. Nano-graphene induced positive effects on methanogenesis in anaerobic digestion. *Bioresour. Technol.* **2017**, *224*, 41–47. [[CrossRef](#)]
28. Yan, W.; Lu, D.; Liu, J.; Zhou, Y. The interactive effects of ammonia and carbon nanotube on anaerobic digestion. *Chem. Eng. J.* **2019**, *372*, 332–340. [[CrossRef](#)]

29. Wang, P.; Zheng, Y.; Lin, P.; Li, J.; Dong, H.; Yu, H.; Qi, L.; Ren, L. Effects of graphite, graphene, and graphene oxide on the anaerobic co-digestion of sewage sludge and food waste: Attention to methane production and the fate of antibiotic resistance genes. *Bioresour. Technol.* **2021**, *339*, 125585. [[CrossRef](#)]
30. Lin, R.; Cheng, J.; Zhang, J.; Zhou, J.; Cen, K.; Murphy, J.D. Boosting biomethane yield and production rate with graphene: The potential of direct interspecies electron transfer in anaerobic digestion. *Bioresour. Technol.* **2017**, *239*, 345–352. [[CrossRef](#)]
31. Casals, E.; Barrena, R.; Gonzalez, E.; Font, X.; Sánchez, A. Historical Perspective of the Addition of Magnetic Nanoparticles Into Anaerobic Digesters (2014–2021). *Front. Chem. Eng.* **2021**, *3*, 745610. [[CrossRef](#)]
32. Ragasri, S.; Vasa, T.N.; Sabumon, P.C. A mini review on effect of nano particles of Fe in the anaerobic digestion of waste activated sludge. *Mater. Today Proc.* **2022**, *51*, 1482–1488. [[CrossRef](#)]
33. Baniamerian, H.; Ghofrani-Isfahani, P.; Tsapekos, P.; Alvarado-Morales, M.; Shahrokhi, M.; Angelidaki, I. Multicomponent nanoparticles as means to improve anaerobic digestion performance. *Chemosphere* **2021**, *283*, 131277. [[CrossRef](#)] [[PubMed](#)]
34. Zhang, B.; Tang, X.; Fan, C.; Hao, W.; Zhao, Y.; Zeng, Y. Cationic polyacrylamide alleviated the inhibitory impact of ZnO nanoparticles on anaerobic digestion of waste activated sludge through reducing reactive oxygen species induced. *Wat. Res.* **2021**, *205*, 117651. [[CrossRef](#)] [[PubMed](#)]
35. Ajaya, C.M.; Mohana, S.; Dinesha, P.; Rosen, M.A. Review of impact of nanoparticle additives on anaerobic digestion and methane generation. *Fuel* **2020**, *277*, 118234. [[CrossRef](#)]
36. Baniamerian, H.; Ghofrani-Isfahani, P.; Tsapekos, P.; Alvarado-Morales, M.; Shahrokhi, M.; Vossoughi, M.; Angelidaki, I. Application of nano-structured materials in anaerobic digestion: Current status and perspectives. *Chemosphere* **2019**, *229*, 188–199. [[CrossRef](#)]
37. Peng, H.; Zhang, Y.; Tan, D.; Zhao, Z.; Zhao, H.; Quan, X. Roles of Magnetite and Granular Activated Carbon in Improvement of Anaerobic Sludge Digestion. *Bioresour. Technol.* **2018**, *249*, 666–672. [[CrossRef](#)]
38. Chen, J.L.; Steele, T.W.J.; Stuckey, D.C. The Effect of Fe<sub>2</sub>NiO<sub>4</sub> and Fe<sub>4</sub>NiO<sub>4</sub>Zn Magnetic Nanoparticles on Anaerobic Digestion Activity. *Sci. Total Environ.* **2018**, *642*, 276–284. [[CrossRef](#)]
39. Chen, R.; Konishi, Y.; Nomura, T. Enhancement of Methane Production by *Methanosarcina Barkeri* Using Fe<sub>3</sub>O<sub>4</sub> Nanoparticles as Iron Sustained Release Agent. *Adv. Powder Technol.* **2018**, *29*, 2429–2433. [[CrossRef](#)]
40. Cheng, J.; Li, H.; Ding, L.; Zhou, J.; Song, W.; Li, Y.-Y.; Lin, R. Improving hydrogen and methane co-generation in cascading dark fermentation and anaerobic digestion: The effect of magnetite nanoparticles on microbial electron transfer and syntrophism. *Chem. Eng. J.* **2020**, *397*, 125394. [[CrossRef](#)]
41. Kouas, M.; Torrijos, M.; Sousbie, P.; Harmand, J.; Sayadi, S. Modeling the anaerobic co-digestion of solid waste: From batch to semi-continuous simulation. *Bioresour. Technol.* **2019**, *274*, 33–42. [[CrossRef](#)] [[PubMed](#)]
42. Ruffino, B.; Fiore, S.; Roati, C.; Campo, G.; Novarino, D.; Zanetti, M. Scale effect of anaerobic digestion tests in fed-batch and semi-continuous mode for the technical and economic feasibility of a full scale digester. *Bioresour. Technol.* **2015**, *182*, 302–313. [[CrossRef](#)] [[PubMed](#)]
43. Li, Y.; Zhang, R.; He, Y.; Zhang, C.; Liu, X.; Chen, C.; Liu, G. Anaerobic co-digestion of chicken manure and corn stover in batch and continuously stirred tank reactor (CSTR). *Bioresour. Technol.* **2014**, *156*, 342–347. [[CrossRef](#)] [[PubMed](#)]
44. Khoufi, S.; Louhichi, A.; Sayadi, S. Optimization of anaerobic co-digestion of olive mill wastewater and liquid poultry manure in batch condition and semi-continuous jet-loop reactor. *Bioresour. Technol.* **2015**, *182*, 67–74. [[CrossRef](#)] [[PubMed](#)]
45. Begum, S.; Das, T.; Anupouju, G.R.; Eshtiaghi, N. Solid-state anaerobic co-digestion of food waste and cardboard in a pilot-scale auto-fed continuous stirred tank reactor system. *J. Clean. Prod.* **2021**, *289*, 125775. [[CrossRef](#)]
46. Zhang, L.; Li, F.; Kuroki, A.; Loh, K.C.; Wang, C.H.; Dai, Y.; Tong, Y.W. Methane yield enhancement of mesophilic and thermophilic anaerobic co-digestion of algal biomass and food waste using algal biochar: Semi-continuous operation and microbial community analysis. *Bioresour. Technol.* **2020**, *302*, 122892. [[CrossRef](#)]
47. Baek, G.; Kim, J.; Lee, C. A long-term study on the effect of magnetite supplementation in continuous anaerobic digestion of dairy effluent—Enhancement in process performance and stability. *Bioresour. Technol.* **2016**, *222*, 344–354. [[CrossRef](#)]
48. Romero-Güiza, M.S.; Vila, J.; Mata-Alvarez, J.; Chimenos, J.M.; Astals, S. The role of additives on anaerobic digestion: A review. *Renew. Sust. Energ. Rev.* **2016**, *58*, 1486–1499. [[CrossRef](#)]
49. Juntupally, S.; Begum, S.; Arellia, V.; Mamindlapell, N.K.; Srinivasan, S.; Anupouja, G.R. Evaluating the impact of Iron Oxide nanoparticles (IO-NPs) and IO-NPs doped granular activated carbon on the anaerobic digestion of food waste at mesophilic and thermophilic temperature. *J. Environ. Chem. Eng.* **2022**, *10*, 107388. [[CrossRef](#)]
50. Dong, D.; Choi, O.K.; Lee, J.W. Influence of the continuous addition of zero valent iron (ZVI) and nano-scaled zero valent iron (nZVI) on the anaerobic biomethanation of carbon dioxide. *Chem. Eng. J.* **2022**, *430*, 132233. [[CrossRef](#)]
51. Zhang, Z.; Guo, L.; Wang, Y.; Zhao, Y.; She, Z.; Gao, M.; Guo, Y. Application of iron oxide (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles during the two-stage anaerobic digestion with waste sludge: Impact on the biogas production and the substrate metabolism. *Renew. Energy* **2020**, *146*, 2724–2735. [[CrossRef](#)]
52. Zhong, D.; Li, J.X.; Ma, W.C.; Qian, F.Y. Clarifying the synergetic effect of magnetite nanoparticles in the methane production process. *Environ. Sci. Pollut. Res.* **2020**, *27*, 17054–17062. [[CrossRef](#)] [[PubMed](#)]
53. Xiang, Y.P.; Yang, Z.H.; Zhang, Y.R.; Xu, R.; Zheng, Y.; Hu, J.H.; Li, X.Y.; Jia, M.Y.; Xiong, W.P.; Cao, J. Influence of nanoscale zero-valent iron and magnetite nanoparticles on anaerobic digestion performance and macrolide, aminoglycoside, beta-lactam resistance genes reduction. *Bioresour. Technol.* **2019**, *294*, 122139. [[CrossRef](#)]

54. Ahmad, A.; Reddy, S.S. Performance evaluation of upflow anaerobic sludge blanket reactor using immobilized ZnO nanoparticle enhanced continuous biogas production. *Energy Environ.* **2020**, *31*, 330–347. [[CrossRef](#)]
55. Cui, P.; Ge, J.; Chen, Y.; Zhao, Y.; Wang, S.; Su, W. The Fe<sub>3</sub>O<sub>4</sub> nanoparticles-modified mycelium pellet-based anaerobic granular sludge enhanced anaerobic digestion of food waste with high salinity and organic load. *Renew. Energy* **2022**, *185*, 376–385. [[CrossRef](#)]
56. Hassanein, A.; Keller, E.; Lansing, S. Effect of metal nanoparticles in anaerobic digestion production and plant uptake from effluent fertilizer. *Bioresour. Technol.* **2021**, *321*, 124455. [[CrossRef](#)]
57. Grosser, A.; Grobelak, A.; Rorat, A.; Courtois, P.; Vandenbulcke, F.; Lemièrre, S.; Guyoneaud, R.; Attard, E.; Celary, P. Effects of silver nanoparticles on performance of anaerobic digestion of sewage sludge and associated microbial communities. *Renew. Sust. Energ. Rev.* **2021**, *171*, 1014–1025. [[CrossRef](#)]
58. Ramos-Ruiz, A.; Sesma-Martin, J.; Sierra-Alvarez, R.; Field, J.A. Continuous reduction of tellurite to recoverable tellurium nanoparticles using an upflow anaerobic sludge bed (UASB) reactor. *Wat. Res.* **2017**, *108*, 189–196. [[CrossRef](#)]
59. Tsui, T.-H.; Zhang, L.; Lim, Y.; Lee, J.T.E.; Tong, Y.W. Timing of biochar dosage for anaerobic digestion treating municipal leachate: Altered conversion pathways of volatile fatty acids. *Bioresour. Technol.* **2021**, *335*, 125283. [[CrossRef](#)]
60. Tsui, T.-H.; Zhang, L.; Zhang, J.; Yanjun, D.; Tong, Y.W. Engineering interface between bioenergy recovery and biogas desulfurization: Sustainability interplays of biochar application. *Renew. Sust. Energ. Rev.* **2022**, *157*, 112053. [[CrossRef](#)]
61. Nizam, N.U.M.; Hanafiah, M.M.; Woon, K.S. A Content Review of Life Cycle Assessment of Nanomaterials: Current Practices, Challenges, and Future Prospects. *Nanomaterials* **2021**, *11*, 3324. [[CrossRef](#)] [[PubMed](#)]
62. Stoycheva, S.; Zabeo, A.; Pizzol, L.; Hristozov, D. Socio-Economic Life Cycle-Based Framework for Safe and Sustainable Design of Engineered Nanomaterials and Nano-Enabled Products. *Sustainability* **2022**, *14*, 5734. [[CrossRef](#)]
63. Xu, W.; Yang, T.; Liu, S.; Du, L.; Chen, Q.; Li, X.; Dong, J.; Zhang, Z.; Lu, S.; Gong, Y.; et al. Insights into the Synthesis, types and application of iron Nanoparticles: The overlooked significance of environmental effects. *Environ. Int.* **2022**, *158*, 106980. [[CrossRef](#)]
64. Markeb, A.A.; Llimós-Turet, J.; Ferrer, I.; Blánquez, P.; Alonso, A.; Sánchez, A.; Moral-Vico, J.; Font, X. The use of magnetic iron oxide based nanoparticles to improve microalgae harvesting in real wastewater. *Wat. Res.* **2019**, *159*, 490–500. [[CrossRef](#)] [[PubMed](#)]
65. Suanon, F.; Sun, Q.; Mama, D.; Li, J.; Dimon, B.; Yu, C.-P. Effect of nanoscale zero-valent iron and magnetite (Fe<sub>3</sub>O<sub>4</sub>) on the fate of metals during anaerobic digestion of sludge. *Wat. Res.* **2016**, *88*, 897–903. [[CrossRef](#)]