Impact of Metallic Nanoparticles on Anaerobic Digestion: a Systematic Review

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Abstract

Anaerobic digestion (AD) is one of the most energy-efficient waste treatment technologies for biodegradable wastes. Owing to the increasing trend of metallic nanoparticle applications in industry, they are ubiquitous to the waste streams, which may lead to remarkable impacts on the performance of the AD process. This review addresses the knowledge gaps and summarises the findings from the academic articles published from 2010 to 2019 focusing on the influences on both AD processes of biochemical hydrogen-generation and methane-production from selected metallic nano-materials. Both qualitative and quantitative analyses were conducted with selected indicators to evaluate the metallic nanoparticles' influences on the AD process. The selected metallic nanoparticles were grouped in the view of their chemical formulations aiming to point out the possible mechanisms behind their effects on AD processes. In summary, most metallic nanoparticles with trace-element-base (e.g. iron, cobalt, nickel) have positive effects on both AD hydrogen-generation and methane-production processes in terms of gas production, effluent quality, as well as process optimisation. Within an optimum concentration, they serve as key nutrients providers, aid key enzymes and co-enzymes synthesis, and thus stimulate anaerobic microorganism activities. As for the nano-additives without trace-element base, their positive influences are relied on providing active sites for the microorganism, as well as absorbing inhibitory factors. Moreover, comparisons of these nano-additives' impacts on the two gas-production phases were conducted, while methane-production phases are found to be more sensitive to additions of these nanoparticles then hydrogen-production phase. Research perspectives and research gaps in this area are discussed.

Keywords: Anaerobic digestion, metallic additives, nano-additives, nanoparticles

1 Introduction

Anaerobic digestion (AD) is a complex anoxic biochemical process that converts biomass or organic waste into biogas and nutrient-rich digestate. The nutrient-rich digestate product is also known as effluent. Based on the main metabolic groups of microorganisms involved, the AD process can be divided into four stages: hydrolysis, fermentation or acidogensis, acetogenesis, and methanogenesis (Fig. 1) (Arif et al., 2018). Considering its energy input and recovery, as well as impacts on the environment, AD is one of the most cost-effective applications among all the biodegradable waste disposal technologies (Khalid et al., 2011; Sawatdeenarunat et al., 2015; Zhen et al., 2017).

Direct (Fig.1A) and indirect (Fig.1B) inhibition factors affect both the stability and efficiency of AD processes, which may consequently lead to failure of the AD process (Fagbohungbe et al., 2017). Moreover, though liquid digestate from anaerobic digesters can be used as liquid fertiliser, which provides essential nutrients for plant growth and maintaining soil ecosystem (Montemurro et al., 2010; Qin et al., 2015), it may also cause leaching of the nitrogen and volatilisation of large amounts of ammonia (over 85% of the ammonium inside the effluent becomes ammonia through direct land application) (Rehl and Müller, 2011), owing to the fast release of this nutrient by diffusion (Fagbohungbe et al., 2017). This type of liquid fertiliser also causes the release of pathogens and heavy metals (Demirel et al., 2013; Fagbohungbe et al., 2017). Whilst the gas state output (biogas) always requires post-treatment to remove impurities, such as hydrogen sulphide (Seadi et al., 2008). Previous studies (Fagbohungbe et al., 2017; Osuna et al., 1997) have reported that the applications of some additives, such as micro-nutrients (MNs) and nano-materials could optimise the AD process by absorbing inhibitory factors and pathogens, thus enhance biogas production and effluent quality.

The additions of metallic micro-nutrients, especially trace elements and their composites could effectively enhance AD performance (Osuna et al., 1997). Since MNs provide essential constituents for enzymes and co-enzymes, it can stimulate microbial bioactivity and microbial growth rate (Mao et al., 2015; Osuna et al., 1997; Qiang et al., 2013). Recent studies have shown that the supplementations of nano-additives cause more obvious impacts on digesters in relation to biogas yield and methane content than those in micrometric size under the same dosage condition (Juntupally et al., 2017). Due to larger surface area to volume ratio, better specificity, more capable of self-assembly, and dispensability, this type of nano-scaled additive exhibited higher reactivity in comparison with MNs (Abdelsalam et al., 2017a).

On the other hand, as a type of ultrafine materials, nanoparticles are not easy to be separated from biodegradable wastes, which may subsequently cause accumulation of inorganic pollutants (usually heavy metals) inside anaerobic digesters. The heavy metals are non-biodegradable, as a result, the AD process cannot effectively remove them from feedstock (Chipasa, 2003). Most of the escaped inorganic pollutants from treatment plants are directly disposed through land applications or released into the water cycle, threatening the aquatic ecosystem and human health (Ni et al., 2019). In addition, due to the toxicity of heavy metals to microorganisms, even low concentrations of metals can inhibit the AD process (Karvelas et al., 2003; Lee et al., 2018; Zayed and Winter, 2000).

Application of metallic nano-additives can be either dosed at a single point in one-stage AD systems together with feedstock or dosed twice in two-stage AD systems in which the first dosage at the beginning for AD acidogensis phase, whilst the second dosage after AD fermentation for the methane production process. The additions of some nano-additives, such as nano-scaled iron and its oxides, induce remarkable enhancements under both of the abovementioned scenarios at very low concentrations (approximately 10mg/L), stimulating activities of microorganisms and key enzymes (Lei et al., 2018; Zaidi et al., 2018; Zhang et al., 2018), therefore leading to more gas production, as well as better effluent quality. In fact, most of the nano-additives are capable to absorb inhibitory compounds including heavy metals, and trap these compounds on their surface (Lei et al., 2018; J. Zhang et al., 2019).

To date, there are no systematic reviews regarding metallic nanoparticles and their impacts on the whole AD process, which can be further separated into the fermentation stage and methane-production phase. Moreover, no reviews in this area took both effluent quality and process optimisation into account. Considering the increasing attention towards organic waste streams, and the significant effects of nanoparticles (NPs) on biochemical processes, this review aims to summarise the findings of academic articles published between 2010 to 2019 on applications of metallic nano-materials in the AD process. Meanwhile, the objective of this review is to provide insights to the influences released by selected metallic nanoparticles on the AD process in terms of gas yield (bio-hydrogen from fermentation phase, methane, carbon dioxide, and hydrogen sulphide for the overall AD process), effluent quality, as well as their influences on fundamental mechanisms, such as pH, chemical oxygen demand (COD), volatile fatty acids (VFAs) production and oxygen-reduction potential (ORP). Finally, the research gaps in this area have been reviewed, and the suggested perspectives have been listed.

2 Approach

In this study, academic publications related to impacts on anaerobic digestion from metallic nanoparticles released between January 2010 and October 2019 were included. The literature search was conducted with English as searching language in October 2019 using Google Scholar and Science Direct.

Fig. 2 summarised the process of literature search and research framework of this review. The search keywords were set according to the types of metallic nanoparticles and research interests on different AD phases. While the types of metallic nanoparticles included in this study were first categorized based on their chemical components, followed by classification of the research interests on different phases of AD processes. Over 1000 papers were retrieved with the searching keywords. A refined search with modified keywords to remove irrelevant publications was then conducted. Afterwards, the titles and abstracts of all the searched publications were manually screened, which duplicates, repeated and irrelevant publications were removed. In the end, full texts of the remaining publications were reviewed to match the inclusive criteria, and targeted searches were carried out to ensure covering all the publications in this area.

2.1 Classification of metallic nanoparticles

The types of metal nanoparticles conducted in this review were selected based on the list of nano-materials either currently used for commercial or being produced in significant quantities for research or developmental purposes (Lovestam et al., 2010). The categories of the nanoparticles were first selected based on their chemical components, then further classified by their known impacts on microorganisms as 'trace-element-based' and 'non-trace-element-based'. For example, both nano zero-valent iron (nano-Fe^0) and nano spinel ferrite (nano-AFe_2O_4, where A stands for metals, such as cobalt and zinc) were categorised under 'iron-based' nano-additives, and grouped into 'trace-element-based' nanoparticles together with zinc-based nano-additives subsequently. In total twenty-three types of metallic nanomaterials are covered in this review, the detailed categories, as well as their abbreviations used in the following sections are presented in Table S.1.

2.2 Search strategy

Applications of metallic nanoparticles could be either in one-stage or two-stage AD systems with fermentation and methane-production phase (Bharathiraja et al., 2016; Ding et al., 2010; Hallenbeck, 2009). The research interests of impacts from metallic nano-materials on the AD process mainly focused on the AD fermentation and methane-production process. In this case, the methane-production process might either refer to the overall AD process for a one-stage AD system, or the methane-production phase in a two-stage AD system. Thereby, the initial search keywords for this review were set as a combination of three terms: anaerobic digestion, research interests on AD phases, together with types of metallic nanoparticles. For example, the following search strategy was used to identify academic publications till the end of 2019 about the zinc-based nano-materials influences on the AD fermentation phase:

> Search keywords in title and abstract of academic papers: ("anaerobic digestion") AND ("fermentation" OR "hydrogen production" OR "bio-hydrogen") AND ("nano zinc").

The second search term related to research interests was set to "methane" OR "biogas" when searching publications focused on in the methane-production process. All the search results were narrowed to academic publications written in English, whilst a large number of publications about iron-based nanoparticles were found irrelevant with the attraction of this review. With refined search keywords for iron-based nanoparticles, the third search term about types of nano-material was changed to "nano" AND "zero-valent iron" OR "ferric" OR "magnetite" OR "spinel ferrite" OR "iron oxide". While the third search term of aluminium-oxide nanoparticles was updated to "nano" AND "alumina". Duplicates were then removed (89 publications), and 151 publications were excluded from this review after manually screening their abstracts. These were publications mainly focused on the fate of nanoparticles inside anaerobic digesters, or tested with unknown source of feedstock and inoculum, or experiments ran without temperature control. In this stage, the following inclusive criteria were used to screen the full text of the remaining 94 publications:

1. Full text is available, with at least methodology section, as well as primary or secondary data;
2. At least the impacts on the volume of harvested gas were mentioned, with either the roles of nano-materials in AD processes, or influences on effluent quality referred to as supplementary information in the publications;
3. The exact sizes of nanoparticles applied in its corresponding research were stated, and within the range listed in the following criteria;
4. Considering the narrow size range of the nanoparticles (1-100nm), and limitations in synthesis and storage of them, this review includes results from publications with the size of additives below 400nm.

After removing repeated publications, a total of 67 research articles were identified that matched the criteria and were saved for further data extraction eventually. In addition, 4 publications were manually added into this systemic review by targeted search, which were cited by the existing selected publications.

2.3 Data extraction procedure

Both qualitative and quantitative analysis of this review were developed based on the data extraction from the selected publications. The main outcomes of the analysis and summary tables of data extraction are presented in the Section of Results and Discussion. For each publication, the following information was recorded for further analysis:

1. Publications year;
2. Characteristics of applied nano-materials, including their chemical forms and sizes;
3. Reported concentrations of the nano-material dosage, that have remarkable influences on the AD process, either they were positive or negative;
4. Operation conditions of the AD systems, including types of substrates and inoculum, temperature, as well as operation time;
5. Main results.

More specifically, data extracted from the main results of each selected paper for structured analysis were summarised into three key themes to modify the metallic nano-materials effects on AD systems. The key themes including impacts on gas production and effluent quality, as well as nano-materials roles on the AD process. Based on the studies by Bajpai et al. (2017) and Alvarado et al. (2014), in total 29 indicators were selected to evaluate the impacts from these metallic nano-additives on the key themes, with more details presented in Table S.2.

2.4 Limitations

This review contained several unavoidable limitations during search and results from synthesis processes, though these processes were designed to be as comprehensive as possible. One of the main limitations of this review is that it only includes publications written in English. Moreover, since the choice of concentration units of nano-materials additions and indicators to modify the AD process, as well as the selection of feedstock and inoculum, vary between publications. Therefore, direct comparisons cannot be made, which means the results of this paper cannot be used to sum up the entire research area. Finally, as the publications without stating exact sizes of the applied nano-materials, the results from these publications were excluded from the analysis of this review.

3 Results and Discussion

3.1 Categorisation of the Content

Fig. 3 shows the counts of publications of metallic nanoparticles interested in this review with categories based on their chemical formations. The most studied nano-material is nano-ZnO (in total 17 publications), followed by nano zero-valent iron and nano-Fe_3O_4 (both had 15 publications). While at the sub-category level, in total 44 publications researched the group of iron-based nanoparticles, 16 publications tested zinc-based nanoparticles, and 8 publications studied titanium-based nanoparticles, respectively. Several sub-categories of metallic nano-materials, such as molybdenum- and manganese-based nano-materials only got 1 publication in the past 10 years. Among the selected 71 publications, over half of them (52%) evaluated the impacts from at least two types of nanomaterials, whilst 4 of them focusing on AD systems amended by multi-nano-additives. It should be mentioned that only Fig. 3 was constructed based on all the selected publications. Whilst the other quantity analyses conducted in this section were developed with separated research interests, with terms “methane-production process” covered both the overall AD process in a single-stage AD system, and methane-production phases in a two-stage AD system.

3.1.1 Operation Conditions

Anaerobic digesters can be used to treat all the biodegradable wastes, and transform them into biogas and liquid effluent under three different temperature conditions (ambient, mesophilic and thermophilic) (Arif et al., 2018). Among all the included studies, most experiments (64% for AD fermentation phase, 91% for methane-production and overall AD processes) were conducted under mesophilic conditions (Fig. S.1).

Apart from operation temperature, the selection of feedstock (e.g. choice of substrate and inoculum, a combination of substrate and inoculum, as well as substrate to inoculum ratio) was recognised as another important factor that may lead to varying in influences on AD amended with the same metallic nano-material. Six combinations of substrate and inoculum have been implemented by researchers studying metallic nano-materials impacts on the AD fermentation phase. Among these selections, the combination of growth medium and single strain hydrogen-producing bacteria (over 30%), such as *Clostridium* and *Enterobacter*, was the most commonly used feedstock, followed by the combination of growth medium and mixed culture bacteria from wastewater treatment plants (over 20%) (Fig. S.2). Moreover, anaerobic sludge applied for the tests on AD fermentation was usually amended with a heat pre-treatment for the enrichment of hydrogen-producing bacteria (Gadhe et al., 2015).

As for the studies focused on methane-production processes, in total 33 combinations of feedstock and inoculum were implemented by the researchers. Whilst 21 types of feedstock only contain one publication for each type, and thus categorised in a group of ‘Other’ in Fig. S.2. Among these feedstocks, the combination of model growth medium and anaerobic granular sludge (over 10%) was the most popular feedstock, followed by pure animal manure (10%), pure waste activated sludge (7.3%) and combination of animal manure and effluent from anaerobic digesters (7.3%).

Comparing with the studies on the AD fermentation phase, it is rare to see the research interested in methane-production processes applying single strain methane-producing bacteria and growth medium. Instead, half of the experiments used substrate from wastewater treatment plants, and effluent or sludge from anaerobic digesters as inoculum. Furthermore, the components of the growth medium were slightly different from the abovementioned growth medium prepared for AD fermentation phase, which contained selected individual VFAs, such as acetic acids (Gonzalez-Estrella et al., 2013).

3.1.2 Studies on influences on AD process and research trends

There is an increasing trend in the number of publications studied metallic nanoparticles influences on the performance of AD systems since 2010, with a major peak in 2015 (Fig. S.3). Over 80% of the studies (59 out of 71) selected in this review focuses on the methane-production phase and the overall AD processes, while the remaining 12 articles focus on the metallic nanoparticle effects on AD fermentation phase.

A range of indicators was used to identify and qualify the impacts on AD systems from metallic nano-materials for both research interests (Fig. S.4). A total number of 9 indicators were implemented for the performance of the AD fermentation phase, whereas 23 indicators were applied for the performance of methane-production processes. In terms of quality of outputs, most studies measured the volume of gas production, including bio-hydrogen yield (67% for studies interested in AD fermentation phase) and bio-methane yield (74% for studies focused on the methane-production process). On the other hand, researches tend to focus more on effluent quality from the AD fermentation phase than it on methane-production and overall AD processes.

Interestingly, 67% of the studies interested in the AD fermentation phase measured final total or individual VFAs concentrations for effluent quality. In contrast, the chemical oxygen demand removal rate is the most studied indicator for effluent quality of the methane-production process, but it was only used in 11.8% of the total number of publications. In addition, for both research interests, most indicators (7 out of 9 for AD fermentation phase, 13 out of 23 for methane-production process) were included to measure influences on AD process.

In the following sub-sections, the impacts on AD processes from metallic nanoparticles are summarised and discussed based on the research interests (AD fermentation phase, as well as methane-production and overall AD processes). Furthermore, a separate sub-section for the co-additives system was summarised (see sub-section 3.5 for more details) in which four articles mentioned the additions of multi-metallic-nanoparticles are reviewed.

3.2 Influences on AD Fermentation Phase

Owing to variances in the dominant microbial communities and the responsible enzymes of these two research interests, the influences from the same metallic nanoparticles on the AD fermentation phase, as well as the methane-production and overall AD processes may be different. The bio-hydrogen produced from the AD fermentation phase is catalysed by hydrolysis-acidification microorganisms via a redox reaction of proton transfer (Bharathiraja et al., 2016; Ding et al., 2010; Hallenbeck, 2009), which is immediately used by methanogens to form methane in the one-stage AD system. Whilst in the two-stage AD system, the harvested bio-hydrogen can either be used directly as a clean energy source or combined with carbon dioxide to form methane (Dong et al., 2019). Furthermore, the effluent from this process can also be used as feedstock for methane generation for a two-stage AD system (Bharathiraja et al., 2016). Through the AD fermentation phase, enzymes, such as Fe-hydrogenase and Ni-hydrogenase, also play important roles apart from bacteria in stabilising pH and optimising metallic nutrients (Bharathiraja et al., 2016; Sakinah et al., 2017).

Based on the results from quantitative analysis (Fig. 4), among all the tested metallic nano-materials, only nano-Cu was reported to have antagonistic effects on the fermentation stage with all the dosage concentrations (Mohanraj et al., 2016). All the other nano-materials were found to have positive impacts on the utilisation of intermediates (i.e. dissolved biomass after hydrolysis) and final VFA production. Of notice, Hsieh et al., (2016) have reported nano-hematite (nano-γ-Fe_2O_3) slightly hindered the substrate to hydrogen conversion process with dosage over 100 mg/L.

The following Table 1 listed the highest reported concentrations of selected metallic nanoparticles that either lead to the best performance of the AD fermentation phase, or no adverse effects on bio-hydrogen production under mesophilic condition. Whilst the concentrations for "the best performances of AD fermentation phase" means beyond this concentration, the positive impacts on this phase decline or vanish.

Among all the metallic nano-additives, the ones with iron-base presented the highest reported tolerant concentrations to over 150 mg/L. Meanwhile, low concentrations of both nano-ZnO and NiO enhanced the AD fermentation phases slightly without adverse impacts, and the appearance of nano-copper inhibited the AD fermentation phase completely. More details were summarised and discussed in the following sub-sections and Supplementary Documents (see Supplementary Table S.3).

3.2.1 Trace-element-based nano-additives

- **Iron-based nanoparticles**

Published results in the past ten years on AD fermentation from three types of iron-based nanoparticles were assessed, including α-Fe_2O_3, γ-Fe_2O_3, and iron oxide nanoparticles (IONPs). In terms of output quality (i.e. the volume of harvested gas, final total or individual VFA production) and process stability, all the iron-based nano-additives have positive impacts on the performance of AD fermentation. The maximum increase in the volume of bio-hydrogen of 153.3% was reported by amended growth medium and treated anaerobic sludge with 50mg/L IONPs (6.5±3nm). The iron-based nanoparticles play important roles in the enhancement of bio-hydrogen production, because they can release iron cations (Fe^{2+}) to synthesis and stimulate key enzymes, and facilitate electron transfer between the enzymes ferredoxin oxidoreductase and hydrogenase (Hsieh et al., 2016). Furthermore, the enhancement in bio-hydrogen production normally occurs in accordance with increased concentrations of acetate, butyrate, and release of protons through their metabolic pathways (Mohanraj and Kodhaiyolii, 2014). In addition, increased concentration of acetate and butyrate which are known as energy favourable volatile fatty acids (VFAs) for the methane production phase(Wang et al., 2018a), may consequently promote the AD process.

Several factors may affect the influences on AD fermentation phase by iron-based nanoparticles, including types of iron-based nano-additives, pH, as well as the nanoparticles exposure concentrations. As an exception among all the iron-based nanoparticles, the bio-hydrogen generated from feedstock amended by nano zero-valent iron (nZVI) was found largely corresponded with its dissolution into water under anaerobic conditions (as shown in Eq.1) (Huang et al., 2016).

$$\mathrm{Fe}^0 + 2\mathrm{H}_2\mathrm{O} \rightarrow \mathrm{Fe}^{2+} + \mathrm{H}_2 + 2\mathrm{OH}^- \quad \text{Eq.1}$$

As for IONPs, 2 out of 3 studies agreed that the samples amended by them presented a better performance in measurements of final bio-hydrogen production when compared to the ones treated with Iron sulphite ($FeSO_4$). Though both forms of iron can facilitate the activities of ferredoxin, thus accelerate the release of protons via the metabolism of pyruvate, only the groups fed with IONPs shifted the main fermentation pathway from butyrate to acetate/butyrate with higher glucose utilisation efficiency (Mohanraj et al., 2014; Mohanraj and Kodhaiyolii, 2014).

Within the optimum range of pH for the AD fermentation phase from 4 to 10, the decrease in pH results in an increase in the number of ferric cations (Fe^{2+}) released from iron-based nanoparticles and form more bioavailable iron compounds for dominant microorganism communities (Han et al., 2011).

Moreover, the amount of recovered bio-hydrogen was found to linearly correlate with the amount of iron-based nanoparticles added below tolerant concentrations (≤ 200mg/L) (Gadhe et al., 2015). If the dosage of iron-based nanoparticles increases beyond this upper limit (dosage of 1600 mg/L), the reactors still achieved a shorter lag period, but reduced hydrogen contents and overall volumes of the generated gas (Han et al., 2011). Meanwhile, more ethanol and propionate were yielded, but less acetate and butyrate were produced from the digesters amended with a higher concentration. The possible mechanism behind these observations is the release of iron cations, which can stimulate the activities of hydrogen-production bacteria under optimum concentration. However, the presence of iron cations is a double-edged sword that the excessive amount of iron cations beyond the tolerant concentration of the AD bacteria might cause bacterial cell lysis and prevent the process (Han et al., 2011).

- **Zinc-based nanoparticles**

In the case of only one publication was found for zinc-based nanoparticles influences focusing on AD bio-hydrogen production, several studies mentioned this nanoparticle's impacts on AD hydrolysis and acidogensis phase were also included in the discussion. In summary, the addition of low concentrations (10 mg/g VS) of nano-ZnO exhibited positive influences on bio-hydrogen production (Elreedy et al., 2019). The growth in gas production may attribute to the involvement of zinc-dependent enzyme ADH, which can catalyse the conversion between alcohols and aldehydes (Eq. 2) (Elreedy et al., 2019). Regarding the number of microbial copies, the dosage of nano-ZnO enriched the relative abundance of key hydrogen producer *Clostridiales*. At the meantime, *Thermoanaerobacterales* was inhibited, which is known as a group of bacteria that use ADH enzymes to produce ethanol from acetaldehyde. In parallel, a decline in the concentration of acetaldehyde and a rise in acetic acid concentration was observed after an incubation time of 48 hours. This provides substantial evidence of the system utilizing acetaldehyde to produce its corresponding carboxylic acid and protons (H^{+}) Eq.3 (Trifunović et al., 2016).

$$\mathrm{CH_3CHO(acetaldehyde) + NADH + H^+ \leftrightarrow CH_3CH_2OH(ethanol) + NAD^+} \qquad \text{Eq.2}$$

$$\mathrm{CH_3CHO(acetaldehyde) + NAD^+ + H_2O \leftrightarrow CH_3COOH(acetic\ acid) + NADH + H^+} \qquad \text{Eq.3}$$

In terms of the reported highest dosed concentrations, the AD fermentative bacteria are less tolerant of the zinc-based nanoparticles in comparison to the iron-based nanoparticles. This is associated with the antibacterial activities causing by zinc ions (Zn^{2+}) that are released from corrosion and dissolution of zinc nanoparticles. Mu et al. (2012), who studied the influences from nano-ZnO addition to anaerobic granular sludge (AGS), found that once the dosage went beyond 50 mg/g TSS, the nano-ZnO prevented the generation of all the functional groups in extracellular polymeric substances (EPS) except polysaccharide contents. The EPS normally functions as a shield protecting the microorganisms from environmental pollutants. Nonetheless, if the addition of nano-ZnO kept raising to over 100 mg/g TSS, the concentration of Zn^{2+} ions surpassed the chemical adsorption capacity of EPS, which means the EPS no longer trap the cations of released from nano-ZnO and leading to further reduction in EPS production (Mu et al., 2012).

- **Nickel-based nanoparticles**

Similar to the abovementioned zinc-based nanoparticles, all the studies interested in the impacts from nickel-based nanoparticles on the AD fermentation phase focused on the form of nickel oxide (nano-NiO). All the selected publications agreed that the addition of nano-NiO at low concentrations (5 and 10 mg/g VS) have great improvements (over 15%) on the bio-hydrogen production (Elreedy et al., 2019; Gadhe et al., 2015; Sakinah et al., 2017). Nano-NiO serves as a source of Ni^{2+} for several metal-enzymes including [Fe-Ni] hydrogenase and acetyl-CoA synthetase (ACS) (Boer et al., 2014). Hydrogenase catalyses bio-hydrogen production and ACS helps to convert acetyl-CoA to acetate, thus the addition of nano-NiO facilitates the conversion of acetaldehyde to acetyl-CoA (Trifunović et al., 2016).

However, inhibition in AD fermentation system under mesophilic conditions were reported with nano-NiO at a dosage of only 10 mg/L. Compared to the reported inhibition concentration of over 200 mg/L under thermophilic condition, the differences may be caused by: (i) smaller size of nano-NiO used in the mesophilic condition, which corresponded with the rate of releasing Ni^{2+} ions; (ii) utilisation of different substrates, wastewater had a relatively low volatile solid content and COD than that of glucose, which was associated with available biomass for bacteria; and (iii) the shifts of dominant hydrogen-producing bacterial groups under a range of temperature conditions, which led to changes in the upper limit of tolerant concentrations to nickel cations.

In contrast to the aforementioned iron-based nanoparticles, the stimulated impacts on fermentative AD processes are observed at low concentrations, implying the hydrogen-producing bacteria are more sensitive to released Ni^{2+} than iron cations.

3.2.2 Non-trace-element-based nanoparticles

Apart from nano-TiO_2 and nano-Cu, most studied metal-based nanoparticles enhance the performance of AD fermentation at optimum concentrations by accelerating substrates to bio-hydrogen conversion (Pugazhendhi et al., 2019). More specifically, the only one publication interested in nano-TiO_2 reported that it presenting limited influences on bio-hydrogen production (Hsieh et al., 2016), while nano-Cu is found to inhibit AD fermentation at all the dosages (Han et al., 2014; Mohanraj et al., 2016).

The supplement of nano-Cu, declined the overall volume of fermentative bio-hydrogen owing to the release of Cu^{2+} cations (Han et al., 2014; Mohanraj et al., 2016). In addition, the nano-CuO particles provoked a higher level of toxicity on the hydrogen-producing bacteria than the copper salts ($CuSO_4$) (Mohanraj et al., 2016).

Particularly, Zhang et al. (2007) reported that at a concentration of 10nM, the nano-gold particles with a diameter of 5nm have achieved the highest bio-hydrogen production, followed by 10nm-nano and 20nm-nano gold particles. Moreover, an increase in the concentration of acetate, together with a reduction in propionate and ethanol were observed. The findings imply that the smaller-sized nano-Au had greater impacts on altering fermentative type from butyrate only to butyrate/acetate by facilitating the hydrolysis process and stimulating key enzyme activities (Zhang and Shen, 2007).

3.3 Influences on Methane-Production and Overall AD Processes

In the past ten years, the influences from 22 metallic nano-additives on methane-production and overall AD processes were studied by researchers. According to results from quantitative analysis on methane production phase and overall AD process (Fig. 5), apart from nano-zinc, all the nano-additives based with trace elements were found to have positive influences on both methane-production and overall AD processes.

On the contrary, the influences from most (5 out of 9) nano-additives based with non-trace-element were reported only to have adverse impacts on either methane-production phase or overall AD processes. Researchers reported that nano-TiO_2 was capable of enhancing the mitigation of hydrogen sulphide in harvested biogas and facilitating electron transfer between microbial species (Heinlaan et al., 2008; H. Li et al., 2017). Effluent quality was also improved by nano-TiO_2 owing to the increase removal rate of volatile solids. Whilst the impacts from both nano-Al_2O_3 and TiO_2 on the volume of produced gas (highlighted in purple boxes) were presented as “No observed” in the figure, which was due to offset of one study reported positive effects and the other study stated adverse impacts. This difference was associated with the selection of feedstock and dosage concentrations (Farghali et al., 2019; L. Zheng et al., 2019). Nonetheless, nano-silver was reported to have beneficial effects on absorbing inhibitory factors, including excessive amounts of sulphide. The impacts presented as “data missing” were owing to lack of experimental data from the selected publications for nano-additives.

The following Table 2 summarised the reported tolerate concentrations of the selected metallic nanoparticles if they only have adverse effects on either methane production stages and the overall AD processes. The reported concentrations for the metallic nanoparticles with the best performance during the AD process in terms of methane production were also included in this table. Similar to the findings for the AD fermentation phase, most of the nano-additives with iron-base had the highest reported tolerant concentrations up to 20 mg/L. Whilst the appearance of nano-ZnO, as well as the nano-additives based with copper, provoked adverse impacts on the methane-production process at very low concentrations. More details were summarised in Supplementary

Documents (see Supplementary Table S.4), and the mechanisms behind these observations were discussed in the following sub-sections, where the metallic nanoparticles were grouped into "trace-element-based" and "non-trace-element-based".

3.3.1 Trace-element-based nanoparticles

- **Iron-based nanoparticles**

Nano-scaled irons, together with its oxides and other composites, are the most prominent nano-additives used to boost the performance of anaerobic digesters owing to their low price, high conductivity, and strong reactivity, as well as the ability to release metallic nutrients for anaerobic microorganisms (Kato et al., 2012; Yamada et al., 2015; Zhou et al., 2014). All six types of iron nanoparticles have been reported to stimulate the AD process, enhance methane production, and improve effluent quality (Table S.4). The results varied between experiments because of differences in feedstock selection applied nanoparticles types and characteristics, as well as operating conditions. In terms of volume of generated methane, the maximum enhancement (increase by 387.1%) was observed from the groups amended with nZVI (Pan et al., 2019), whilst for nano-Fe_2O_3 the highest improvement was only around 20% (Wang et al., 2016).

Compared with micro-sized iron-based additives, nano-iron-additives has a relatively higher surface-to-volume ratio, larger specific surface area and superior surface reactivity, which can serve to eliminate a wider range of inhibition properties and pollutant species, including high abundance of ammonia, phosphorus and sulphate, together with excessive amounts of heavy metals in wastewater treatment rapidly and thoroughly via precipitation (Tareq W M Amen et al., 2017; Khalil et al., 2017; Wang et al., 2010, 2018b).

Focusing on the utilisation of nZVI in AD systems, 5 out of the selected 14 publications stated that the presence of this nano-additive promoted the hydrolysis-acidification process by enhancing reduction of substrate and facilitated the availability of degradable biomass for anaerobic microorganisms (Abdelsalam et al., 2017b, 2016b; Ma et al., 2019; Pan et al., 2019; Wang et al., 2018b). This is in agreement with the findings of Yu et al. (2016), who observed increasing amounts of dissolved organic matter (DOM) species inside the sludge fermentation liquor amended with nZVI. In subsequent studies, Amen et al. (2018) and Ambuchi et al. (2017) showed that the process of methanogenesis stage was also stimulated, as this nano-additive served as electron donors that could reduce carbon dioxide to methane.

Regarding the microbial community, dosing low concentrations of nZVI (below 200mg/L) (Wu et al., 2013) into the AD system could enrich the relative abundance of functional microorganisms involved in the processes of hydrolysis-acidogensis and methanogenesis (Pan et al., 2019; Wang et al., 2018a). Due to the facts that free sulphate sources in the liquid phase were immobilized by the production of ferrous sulphite (FeS) and pyrite (FeS_2), the populations of sulphate-reducing bacteria (SRB) were decreased (Chaung et al., 2014), which is a group of microorganisms known as competitors of acetogens and methanogens using the same substrates inside anaerobic digesters (Dar et al., 2008). Since SRB is identified as the only biological source of H_2S inside the

AD system (St-Pierre and Wright, 2017), adding nZVI cannot only alter microorganism structure of AD process, but also lower the hydrogen sulphide (H_2S) contents inside biogas,

As a strong reductant (E_h=-0.44V), the supplementation of nZVI into AD systems can rapidly reduce oxidation-reduction potential (ORP) to maintain a reducing environment (Pan et al., 2019), and increase the production of more energy favourable volatile fatty acids (VFAs) like acetic and butyric acids (Wang et al., 2018a). Since both acidogensis phase and reactions between water and Fe^0 particles from the dissolved nZVI can generate hydrogen, which consequently increases hydrogen partial pressure, thus further limiting the production of propionic acid (Wang et al., 2018b). Afterwards, there are two pathways to utilise the produced hydrogen. The community of hydrogenotrophic methanogens catalyses the reaction of hydrogen and carbon dioxide to methane. Alternatively, homoacetogenic archaea first convert the hydrogen to acetate, followed by break-downs of the acetate leading to the rise of final methane contents (Zhen et al., 2015).

The amount of Fe^0 particles dissociated from nZVI is decreased with the increase of particle sizes (Goldstein et al., 1992; Talapin et al., 2001), but positively correlated with the surface-to-volume ratio that highly depends on shapes of the particles (Abbas et al., 2013). In a study focusing on sludge in AD treatment responses to nZVI (5-100nm) and ZVI (100 mesh, around 0.177mm and 1000 mesh, around 0.015mm), all the three sizes of particles enhanced both the overall biogas production and methane yield, in which the 100 mesh ZVI achieved the most cumulative methane volume (Yu et al., 2016). However, only the addition of nZVI successfully reduced the final carbon dioxide contents below that of the control group (Yu et al., 2016). The released Fe^{2+} cations enriched the abundance of dominant hydrolysis-acidification microorganisms, such as *Anaerolineae* and *Clostridia* to generate more hydrogen, therefore stimulated the AD system generating methane from carbon dioxide via the two pathways as described above (Zhen et al., 2015).

On the other hand, the rapid dissolution of nZVI, which not only resulted in overproduction and accumulation of hydrogen that might inhibit acetoclastic methanogens (Zhen et al., 2015), but also led to high abundance of dissolved ferrous ions (Fe^{2+}) (Pan et al., 2019). The excessive amount of Fe^{2+} ions could combine with free phosphate ions (PO_4^{3-}) or thiol groups (R-SH) in the liquid to form stable complexes, hindering the phosphorus and sulphite uptake by methanogenic microbes, therefore inhibiting methanogenesis (Mu and Chen, 2011; Rudnick et al., 1990). Meanwhile, the high concentration of ferrous ions induced the production of reactive oxygen species (ROS) via the Fenton reaction (Tang and Lo, 2013), which were highly toxic to all types of microorganisms. Another possible mechanism behind the negative impacts from this nano-additive is the rapid coating of iron and ferric oxide ($Fe(OH)_3$) on the cells, which induces reductive stress, cell membrane structures disruption and cell lysis (Auffan et al., 2008; Lee et al., 2008; Marsalek et al., 2012).

The adverse effects of nZVI on the activities of microorganisms in anaerobic conditions provide a feasible solution to kill bacteria that carry antibiotic resistance genes (ARGs), and harmful bacteria, such as *Escherichia coli* (*E. coli*) during the AD process. The addition of nZVI could remove ARGs inside AD sludge by reducing amounts of MRGs without affecting the AD processes. Two studies reported that the addition of 80 mg/L nZVI in antibiotics-containing wastewater raised the removal efficiency of ARGs over 50% (Fang et al., 2011; Ma et al., 2019). Nonetheless, the relative abundance of most selected heavy metal resistance genes (MRGs) was simultaneously decreased, which were found having intimate genetic linkage with MRGs (L. G. Li et al., 2017), and horizontal gene transfer through MRGs was recognised as the main mechanism behind the transfer of ARGs between microorganisms (Pruden et al., 2006; Von Wintersdorff et al., 2016). Whereas the activities of the dominant microorganisms were enhanced at the same time, except the bacterial groups of *Firmicutes* (L. G. Li et al., 2017).

Regarding heavy metal removal, only one publication was found. In which, additions of both nZVI and nano-Fe_3O_4 resulted in more than 95% of these heavy metal contents trapped within the solid phase (Suanon et al., 2016). Meanwhile, the concentrations of heavy metals in the forms (water-soluble, exchangeable, and carbonate-bound) that could be easily taken in by plants were significantly reduced. With the same dosage, nZVI had better performance in the removal of heavy metals than nano-Fe_3O_4, which only contributed to immobilisation of the heavy metals by physical and chemical absorptions. Whilst nZVI could trap heavy metals via redox reactions, absorption, and co-precipitation on the oxide shell formed around it (Suanon et al., 2016).

Iron oxide nanoparticles (IONPs) is a combination of maghemite (γ-Fe_2O_3) and magnetite (Fe_3O_4) particles with superparamagnetic properties (Ansari et al., 2019). Both Iron (II, III) oxide (Fe_3O_4) and Iron (III) oxide (Fe_2O_3) were recognised as essential nutrients for anaerobes activities in AD (Romero-güiza et al., 2016; Yang et al., 2013). Under anaerobic conditions, the iron oxides supply both ferrous ions (Fe^{2+}) and ferric ions (Fe^{3+}) slower than the abovementioned nZVI, owing to the fact that they are insoluble in the environment with neutral pH ($pH \approx 7$) (Weber et al., 2006). As a type of conductive material, the IONPs can still function as electron conduits of direct interspecies electron transfer (DIET) in their insoluble state between syntrophic, organic-oxidizing bacterial communities and CO_2-reducing archaea groups (Mattioli and Bolzonella, 2016). Thereby, they can accelerate acetogenesis-methanogenesis, and raise final methane contents at lower concentrations (Wang et al., 2016).

The conductivity of nano-iron oxide was also proven to have effects on the methane-production stage (Kato et al., 2012). Both the conductive (nano-Fe_3O_4) and semi-conductive (nano-Fe_2O_3) nano-additives had similar stimulation impacts on AD, including shorter lag phase and biogas production period, meanwhile boosting the methane production rate. However, the addition of insulative mineral (ferrihydrite) did not share these positive effects (Kato et al., 2012). The findings suggested that DIET was established between *Geobacter* and *Methanosarcina* by utilising conductive particles as electron conduits (Kato and Watanabe, 2010), thereby creating extracellular nanowires between anaerobic bacteria and archaea (Gorby et al., 2006; Reguera et al., 2005). Alternatively, the existence of conductive materials allowed electric syntrophy of microorganisms via direct contact (Agapova et al., 2010).

Utilising spinel ferrite (with a general formula of AFe_2O_4) nanoparticles for anaerobic digesters, especially the ones with trace elements like cobalt ($NiCoFe_2O_4$) and nickel ($NiFe_2O_4$), can produce more biomass for microorganisms and facilitate the activities of microorganisms, therefore increase the final biogas production (Lin et al., 2018). The stimulation impacts from spinel nano-additives released of nickel, cobalt, and iron cations as key factors for the formation of enzymes or coenzymes, as well as essential nutrients for microbes (Romero-güiza et al., 2016; Thauer et al., 2008). On the other hand, the exposure of AD to a strong, constant magnetic field created by nickel-zinc-ferrite nanostructures provoked inhibition of AD efficiency at very low concentrations (7mg/L) (Dębowski et al., 2016; Lin et al., 2018).

All the iron-based nano-additives shared some similar mechanisms behind these positive impacts, including: (i) release of bioavailable iron ions (Fe^{2+} and Fe^{3+}), which is known as an essential nutrient for microbial power generation, DNA replication (Zaidi et al., 2018) and key enzymes formation (Zhang et al., 2018), therefore increase microbial abundance and activities of key enzymes or co-enzymes, (ii) serve as conduits for electrons, hence stimulate electron transfer (both interspecies electron transfer, IET and direct interspecies electron transfer, DIET) between the bacterial and archaeal communities (Lovley, 2017), and (iii) absorb inhibitory compounds and works as a pH buffer, thus stabilise the AD system (Lei et al., 2018; J. Zhang et al., 2019). Finally, all the publications concluded that the influences on the AD process from nano-iron-additives were dosage-dependent. Excessive dosage of iron-based nanoparticles hindered the overall process resulting in reductions of biogas production.

- **Zinc-based nanoparticles**

The antibacterial characteristic of ZnO nanoparticles can be utilized to prevent the growth of coliform bacteria in wastewater treatment (Mostafaii et al., 2017; X. Zheng et al., 2019). Although the addition of nano-zinc into anaerobic digesters does not have direct influences on the structure of bacteria, it still presents inhibitory impacts to the growth of the hydrolysis and acidification bacteria, such as *Firmicutes* and *Bacteroidetes*. The activities of key enzymes and coenzymes, including protease, acetate kinase (AK) and F_{420} are also hindered by the addition of nano-zinc (Zheng et al., 2015). Additionally, the addition of zinc oxide nanoparticles slightly enriched most of the hydrogenotrophic methanogens (Zhao et al., 2019). While all the acetoclastic methanogenesis were prohibited by nano-ZnO besides *Methanosarcinaseae* (Zhao et al., 2019) since the acetoclastic methanogens were more sensitive to this particle compared with hydrogenotrophic methanogens (Gonzalez-Estrella et al., 2013).

The supplementation of nano-ZnO in liquid swine treatment under anaerobic conditions shrunk the volume of emitted hydrogen sulphide (H_2S) in the gas stream by 99% by forming zinc sulphide (ZnS) as described in Eq.4 (Gautam et al., 2017). The produced hydrogen sulphide was first dissolved in water, then dissociated into hydrogen ions (H^+) and bisulphide ions (HS^-). Afterwards, the HS^- anions diffused into the nanoparticles, and were finally chemisorbed by the hydroxide (OH^-) groups on the ZnO particle surface (Song et al., 2013). The overall production of biogas was decreased, with a reduction of 72% of methane (CH_4) and 62% of carbon dioxide (CO_2) volumetrically at the same time(Gautam et al., 2017).

$$\mathrm{ZnO} + \mathrm{H_2S} \rightarrow \mathrm{ZnS} + \mathrm{H_2O} \qquad \text{Eq.4}$$

Most of the existing studies (7 out of 12) found that the influences on the AD process due to exposure of zinc oxide (ZnO) nanoparticles were dosage-dependent. The presence of nano-ZnO at low concentrations in anaerobic digesters did not inhibit their process completely. On the contrary, it was reported to have slightly stimulating effects on protein solubilisation (Zhang et al., 2017). At low concentrations (1mM), though the addition of nano-ZnO gave adverse effects on anaerobic digestion treated model organic wastes, such as a longer lag phase and biogas production period, as well as reduction of maximum daily methane production rate to around half of the control (Zhu et al., 2019). In addition, the AD system can overcome the antagonistic impacts by either absorbing the nanoparticles with organics followed by precipitation, or changing the surface charge of nano-ZnO to neutral or negative. Therefore, after a short (2 days) hinder period the AD system became stable with a slight increase (2.19%) in final methane production (Zhu et al., 2019). Beyond this tolerate concentration, the addition of nano-ZnO blocked the AD process completely due to the change of archaeal community structure and VFA accumulation (Mu et al., 2011).

The main reason for the adverse effects on methane production from the AD system is the release of Zn^{2+} cations from zinc oxide nanoparticles (Mu and Chen, 2011), when its concentration gradually increases during the AD process over time. However, as zinc oxide has low aqueous solubility (Karlsson et al., 2009), the adverse influences on gas production highly rely on the differences in particle surface and characteristics of nano-ZnO once the concentration reached a certain level (Luna-delRisco et al., 2011).

In the only one study related to the removal rate of ARGs after the AD process amended with nano-ZnO, Huang et al. (2019) found that after operation for 100 days, the overall abundance of ARGs increased by 28% comparing with the control sample. Additionally, both abundance and diversities of the mobile genetic elements (MGEs) were increased by the presence of these nanoparticles, which might serve as carriers of the ARGs with better mobility. The exposure of nano-ZnO triggered signal transduction from cell to cell, facilitated horizontal gene transfer (HGT), also enriched some of the genera that acted as hosts of ARGs (Lactones et al., 2004; Tan et al., 2014; Valle et al., 2004).

The toxicity of nano-ZnO on AD microorganisms can be attenuated by co-addition of biogenic or iron sulphide (FeS), leading to a displacement reaction to form zinc sulphide (ZnS) and release of metallic nutrients including iron cations (Fe^{2+}) (Gonzalez-Estrella et al., 2016, 2015b). Alternatively, pre-treat the nano-ZnO in order to immobilize and stabilise them with biogenic solutions, such as sodium alginate solution and methylenebisacrylamide before dosing them at low concentration into the AD system (Ahmad and Reddy, 2019; Gautam et al., 2017). Moreover, in comparison to the wet AD system, the supplementation of nano-ZnO into solid waste anaerobic digesters was less harmful to the process under similar concentrations (Eduok, 2015).

- **Other trace-element-based nanoparticles**

All the metal nano-additives with trace elements present enhancements to the AD process concerning the amount of biomass produced from substrate, VFAs yield, lag phase period, enzymes and co-enzymes production, as well as the volume of gas yield at low concentration. In particular, nano-Co and Ni not only shortened the length of the lag phase, but also increased the time required to achieved the peak of gas production (Abdelsalam et al., 2016b).

The group amended with 2mg/L nano-Co gave adverse influences in the volume of biogas yield, demonstrating slight inhibition on methanogenic microorganisms, while the group treated with nano-Ni at the same concentration generated the most amount of methane, as well as biogas (Abdelsalam et al., 2016b). The experiment using manure as substrate created a sulphite-rich environment (Manitoba Agriculture, 2015), where the dissolved amount of measured cobalt cations was significantly higher than the estimated concentration based on the equilibrium constant (Gustavsson et al., 2013). Furthermore, the high sulphite content in AD sludge may cause the formation of metal sulphites, and thus lead to sulphide precipitation and restrains in trace element potential bioavailability. The bioavailability and bioreactivity of metallic nutrients to microorganisms is tightly associated with the metal fractions. Whilst the accessibility of metal fractions is in order of water-soluble, exchangeable, acid-soluble, oxidizable (organic and sulphide-bound), and residual (Jia et al., 2017; Yekta et al., 2017). Base on this fact, the influences on the bioavailability of nickel were lower in sulphite-rich environments, and nickel-sulphite can work as storage of nickel (Jansen et al., 2007) and provide metallic nutrient at a slower pace than cobalt.

With high concentration (500 mg/g TSS) of nano-MgO led to inhibition of the anaerobic digesters treated waste activated sludge completely, and finally led to a reduction of 98.92% in methane production (Wang et al., 2016). The primary reason behind this was the release of excessive amounts of Mg^{2+} cations, which is consistent with damage in cell membranes and loss of key enzymatic activities (Wang et al., 2016).

3.3.2 Non-trace-element-based Nanoparticles

The studies on nano-Ag^0, Al_2O_3, CeO_2, and TiO2 did not report any notable effects on AD performance with the tolerate concentrations up to 1500 mg/L (Gonzalez-Estrella et al., 2013; Mu et al., 2011). In contrast to these findings, Ünşar et al. (Ünşar et al., 2016) reported a slight inhibition from the addition of 150 mg/g TS nano-Ag on AD of waste activated sludge (WAS). The differences in the results might be induced by changes in size ranges and substrate. Whereas, adverse influences from manganese(III) oxide (Mn_2O_3) nanoparticles with high concentrations (1500 mg/L) on methane production was observed, but the mechanisms behind the responses still needed further investigation (Gonzalez-Estrella et al., 2013).

Nano-Cu^0 and nano-CuO caused severe inhibition on methanogenesis that is mainly attributed to the release of Cu^{2+} ions (H. Li et al., 2017). The dosage of 100 mg/L of nano-Cu^0 completely blocked the hydrogenotrophic methanogenesis pathway after two generations, while the methane production from the acetoclastic methanogenic pathway was around half of that of the control group (Gonzalez-Estrella et al., 2013). This result demonstrated that the hydrogenotrophic methanogens were more sensitive to copper cations (Cu^{2+}) (Chen et al., 2008; Luna-delRisco et al., 2011). Moreover, the nitrogen and phosphorus removal efficiencies were evidently affected by high concentrations of nano-CuO addition, as the nanoparticles prevented the activities of enzymes, damaged cell membranes, and thus caused cell lysis of the microorganisms (Wang et al., 2017). Similar to the aforementioned ZnO nanoparticles, nano-CuO at concentrations of 20 mg/g TSS also activated the cell-to-cell signal transfer, especially quorum sensing. While MGEs were enriched and horizontal gene transfer (HGT) was also promoted by nano-CuO, therefore, stimulated the propagation of ARGs (Huang et al., 2019).

Regarding the low dispersion properties of nano-CeO_2 inside the aqueous medium, this type of nanoparticle was more likely to precipitate then dissolve into AD sludge. As a result, the change of reduction in the volume of biogas was insignificant with the increase in the concentration of this type of nano-additive from 100 to 1000 mg/L in the AD of model substrate solution and anaerobic sludge (Nguyen et al., 2015). The upper limit of dosage concentration of nano-CeO_2 for mesophilic AD microorganisms was below 0.16 mg/mL (García et al., 2012). Particularly, nano-CeO_2 at low exposure concentrations could increase the AD performance in terms of biogas yield and removal efficiency of COD in the effluent (Nguyen et al., 2015). The positive impact is believed to be attributed to the released Ce^{4+} and Ce^{3+} ions, which could covert toxic ROS into oxygen and water (Xia et al., 2008).

With regard to the silver-based nanoparticles, despite the toxicity on AD microorganisms from the released Ag^+ ions (Yang et al., 2012a), the surface charge of the particles was another factor affecting their impacts on AD. The nano-Ag with negative or neutral surface charge were stabilised in either solid phase or liquid medium and thus did not inhibit the AD process (Gitipour et al., 2016). Additionally, over 90% of the PVP coated nano-Ag were removed from sludge after AD treatment (Doolette et al., 2013). For the particles with positive surface charge, they were more likely to interact with microorganism communities that were negatively charged, and thus obtained higher toxicity. Moreover, the release of silver cations depleted sulphite existing inside AD sludge by forming Ag_2S, leading to inhibition of the microorganisms that relied on sulphite as essential nutrients (Doolette et al., 2013; Gitipour et al., 2016; Mu and Chen, 2011; Rudnick et al., 1990). As for anaerobic digesters treating dry waste, the addition of nano-Ag at a concentration of 10 mg/kg of solid, caused accumulation of VFAs, and thus reduced the population of archaeal communities, which could not survive in acid environments (Yang et al., 2012b).

As an insoluble nanoparticle, the releasing ion concentration from nano-TiO_2 into aqueous medium is negligible under anaerobic neutral conditions. Hence, it does not present any significant impact on the harvest of bio-hydrogen or biogas (Hsieh et al., 2016). In this case, the possible mechanisms behind the inhibitory impacts are the aggregation of these nanoparticles on the sludge surface, which leads to less active sites and reduced surface area for bacteria responsible for fermentation, hence decreases the viability of biomass for microorganisms in the following phases (Heinlaan et al., 2008; H. Li et al., 2017).

3.4 Comparison of Metallic Nanoparticles Impacts on AD Fermentation, Methane-Production, and Overall AD Processes

Only the impacts from 7 types of metallic nanoparticles were studied for both research interests (AD fermentation phase, methane-production and overall AD processes) in the past ten years. Fig. 6 illustrates the differences between reported tolerate concentrations for both research interests, while all the units for dosage concentration are converted into mg/L. Of notice, the reported tolerate concentration of nano-ZnO still led to adverse effects on the methane-production stage and overall AD process (Zhu et al., 2019), thereby the actual tolerate concentration of nano-ZnO was much lower than 1mM.

Apart from nano-ZnO and nano-Cu, the reported tolerated concentrations of all the metallic nanoparticles for the AD fermentation phase were higher than that of the methane-production stage and overall AD phase. This indicates that the methane-producing archaea, as well as acetogenesis bacteria are more sensitive to the addition of nanoparticles than hydrogen-producing bacteria under the same concentration (H. Li et al., 2017). Furthermore, the presence of nano-Cu prohibited both hydrogen-production and methane-production stages.

3.5 Influences from Multi-nanoparticles

Dosing multi nano-additives, especially nano-additives that are trace elements based, into anaerobic digesters normally provokes synergistic effects, resulting in further improvement in either the AD fermentative system or whole AD process (see Supplementary Table S.5). Moreover, the AD system amended with nano-TiO_2 has been observed to have diminished impacts on inhibition owing to excessive amounts of ZnO nanoparticle addition (L. Zheng et al., 2019).

Co-addition of nano-Fe_2O_3 and nano-NiO incurs enhancement in bio-hydrogen production from AD fermentation of wastewater and anaerobic sludge (Gadhe et al., 2015). With the same exposure concentration of nano-Fe_2O_3, when the concentration of nano-NiO dosed in the multi-nanoparticles system was below 5 mg/L, the amount of bio-hydrogen increased linearly. Whereas, if the nano-NiO loading went over 5 mg/L, the stimulating impacts were prevented, which corresponded with the abovementioned tolerant concentration of nano-NiO in the fermentative AD process (Gadhe et al., 2015).

In comparison to the system amended with single nano-additive, a co-addition system can undertake higher tolerant concentrations for each nano-additive. For instance, Taherdanak et al. (2015) demonstrated inhibitory impacts in AD fermentation with dosages of 25 mg/L nZVI or 25 mg/L nano-Ni^0. However, under co-addition conditions, adding 37.5 mg/L nZVI together with nano-Ni^0 at the same concentration could significantly improve the fermentative performance (Taherdanak et al., 2015). Although adding multi-nanoparticles based with trace elements did not bring striking improvements in methane production, in fact, they caused a notable reduction in hydrogen sulphide contents (Hassanein et al., 2019).

The surface of TiO_2 can serve as a perfect site to absorb free ions in AD sludge that have negative impacts on the process, such as Zn^{2+} via relevant reactions as expressed in Eq. 5, hence attenuating the antagonistic effects from ZnO nanoparticles (Tong et al., 2014). In this case, the AD system applied with both ZnO and TiO_2

nanoparticles presented better performance than the one only supplied with nano-ZnO at the same concentration. The AD system amended with both nanoparticles presented less extracellular LDH production, higher VFAs to the methane consumption rate, as well as increasing acetic acid yield with facilitating influences on the activities of both protease and acetate kinase in comparison with single-additive systems (L. Zhang et al., 2019; L. Zheng et al., 2019). The results further proved that with the help of TiO_2 nanoparticles, the AD system could overcome the inhibitory impacts caused by the presence of ZnO Nanoparticles due to released zinc cations.

$$\mathrm{Zn^{2+}(aq)} + \equiv \mathrm{TiOH(s)} \rightleftarrows \equiv \mathrm{TiOZn^{2+}}(s) + \mathrm{H^{+}}(aq) \qquad \text{Eq. 5}$$

Where ≡ emphasizes that the adsorption occurs on the surface of nano-TiO_2.

4 Summary and Future Research Prospects

Almost all kinds of nano-additives with trace elements have been proved that they can be used to improve AD performances by different approaches at low concentrations, including: (i) altering AD microbial structure; (ii) releasing metallic nutrients; (iii) producing more biomass by facilitating substrate bio-degradability; as well as (iv) absorbing excessive amounts of inhibitory factors like heavy metals. Among them, ZnO nanoparticles and cobalt nanoparticles presented adverse impacts on biogas or methane yield at relatively low dosage concentrations, as the dominant metal fractions of them inside AD can be easily uptaken by microorganisms (in forms of water-soluble, exchangeable, acid-soluble and oxidizable), and thus excesses the tolerance limits.

Meanwhile, the addition of most non-trace elements-based metal nano-additives into the AD process does not show noticeable influences. However, with the increase in concentrations, all of them exhibit negative effects on gas production rate and leading to a reduction in the overall amount of gas yield. The reasons behind the toxic influences may either cause by nanoparticle aggregation, which builds physical barriers on the anaerobic sludge surface to prevent reactions, or due to the release of excessive toxic cations causing production of ROS and damages on cell integrity.

The application of metallic additives in nano-size implies more significant influences on the AD process compare with bulk size additives. The nanoparticles are observed to stick on the surface of anaerobic sludge due to their negative surface charges, then these nanoparticles are easier to penetrate through cell membranes, breakdown complex organics, produce more biomass for microorganisms, and thus facilitate metabolism in the following phases of AD. While the impacts from these metallic nanoparticles on the AD process tightly correspond with their released free ions. While the differences in influences of metallic nanoparticles on the AD process not only associated with the types of species based on chemical forms, but also attributed to a number of factors like particle characteristics (sizes, shapes, surface area, and surface charge), dispersion degree and stability.

Besides, the AD system supplementation with multi-nano-additives achieves better performance with a dramatic increase in methane production or overcome some of the negative impacts. In particular, nano-TiO_2 in the multi-additives system trapped the inhibitory elements, such as excessive amounts of sulphite and zinc ions. Whereas, the system amended with multi-nano-trace element presents synergistic effects.

Future work in this area needs to obtain a better understanding of nano-additives roles in anaerobic digesters and their speciation, together with the factors affecting their bioavailability and bioreactivity through AD process:

1. In most of the current literature, the amount of gas production was used as the only indicator to justify the effects of metal nano-additives on the AD process. As the other important output from anaerobic digesters, the changes in effluent quality after amending with nano-additives requires further investigation. In addition, the researches on change in microbial structure, as well as the quality of the generated gas also need to be taken into account.
2. Most of the studies on nano-additives have carried out by batch experiments. Further studies on feasibility of adding these nano-additives in other anaerobic reactor configurations are required, and experiments operated in different environment need to be addressed clearly.
3. The experiment designs from existing publications are mostly used for indicating the impacts of short-term exposure. However, if the dosed concentration of these nanoparticles is below tolerant concentration, the AD system may require time to recover by themselves. In this case, results from long-term exposure tests are closer to reality, which can be obtained by semi-continuous and continuous tests.
4. Further studies are required to find out the tolerant concentrations of the metallic nanoparticles on AD with different substrate and inoculum regarding volatile solids.
5. A more in-depth study is also required to verify the metal fractions and bioavailability under anaerobic conditions. Moreover, further research on the synergistic effects achieve by multi-nanoparticles on metal specification, especially the formation of metal sulphides in the sulphite-rich environment is also demanded.
6. It is still not clear in the literature about influences due to differences in particle characteristics of nano-additives with the same chemical components, as well as the depression degree and stability of the nanoparticles in the liquid phase. Thereby, a series of experiments should be carried out to determine an optimal size range, the optative shapes, and the best dispersion solution, as well as suitable pre-treatment for each metallic nano-additive.
7. Development of procedures to regulate the studies that justify the nanoparticles' impacts on the AD process and its outputs, including feedstock combinations and indicators selections.
8. Lastly, research is still required on the differences in mechanisms behind the improvement in dark fermentative AD performance with additions of nano-additives with photocatalysis characteristics, such as hematite (α-Fe_2O_3) and titanium oxide (TiO_2), and the ones without this feature.

5 Conclusions

The supplementation of metallic nanoparticles into the AD system presents notable influences on the performance of AD regarding process stability, gas production, as well as effluent quality. Recently, extensive research on impacts on the AD process from these nanoparticles, especially the ones with trace element based have pointed out the feasibility of applying some of them in reality. Nonetheless, the solutions to overcome inhibition from existing nanoparticles inside anaerobic digesters, such as nano-ZnO, Ag, and CuO still need further investigations. As for microbial communities, methane-producing archaea are more sensitive to the addition of nanoparticles than hydrogen-producing bacteria under the same concentration. The toxic impacts of the metallic nanoparticles to AD microorganisms are dosage-dependent and are largely dependent on their characteristics and fractions in AD sludge. By understanding the impacts from both single-addition and co-addition of different metallic-based nanoparticles, some industrial by-products in nanoscale, such as fly ash (FA) can be applied to monitor the performance of anaerobic digesters.

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Figures

Impact of Metallic Nanoparticles on Anaerobic Digestion: a Systematic Review

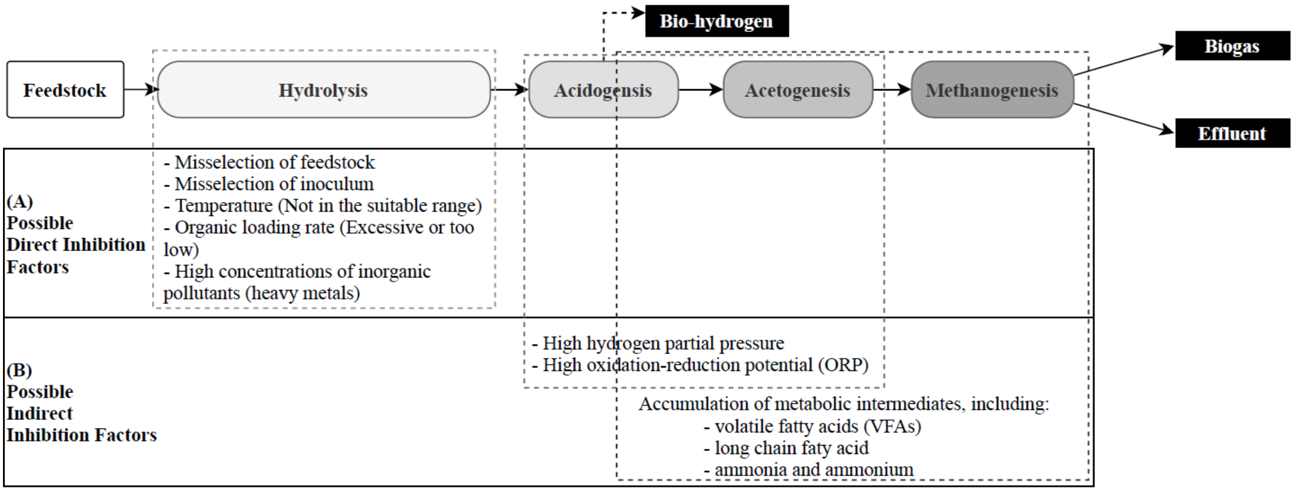

Fig. 1. Phases of AD process with possible inhibition factors and limitations of outputs.

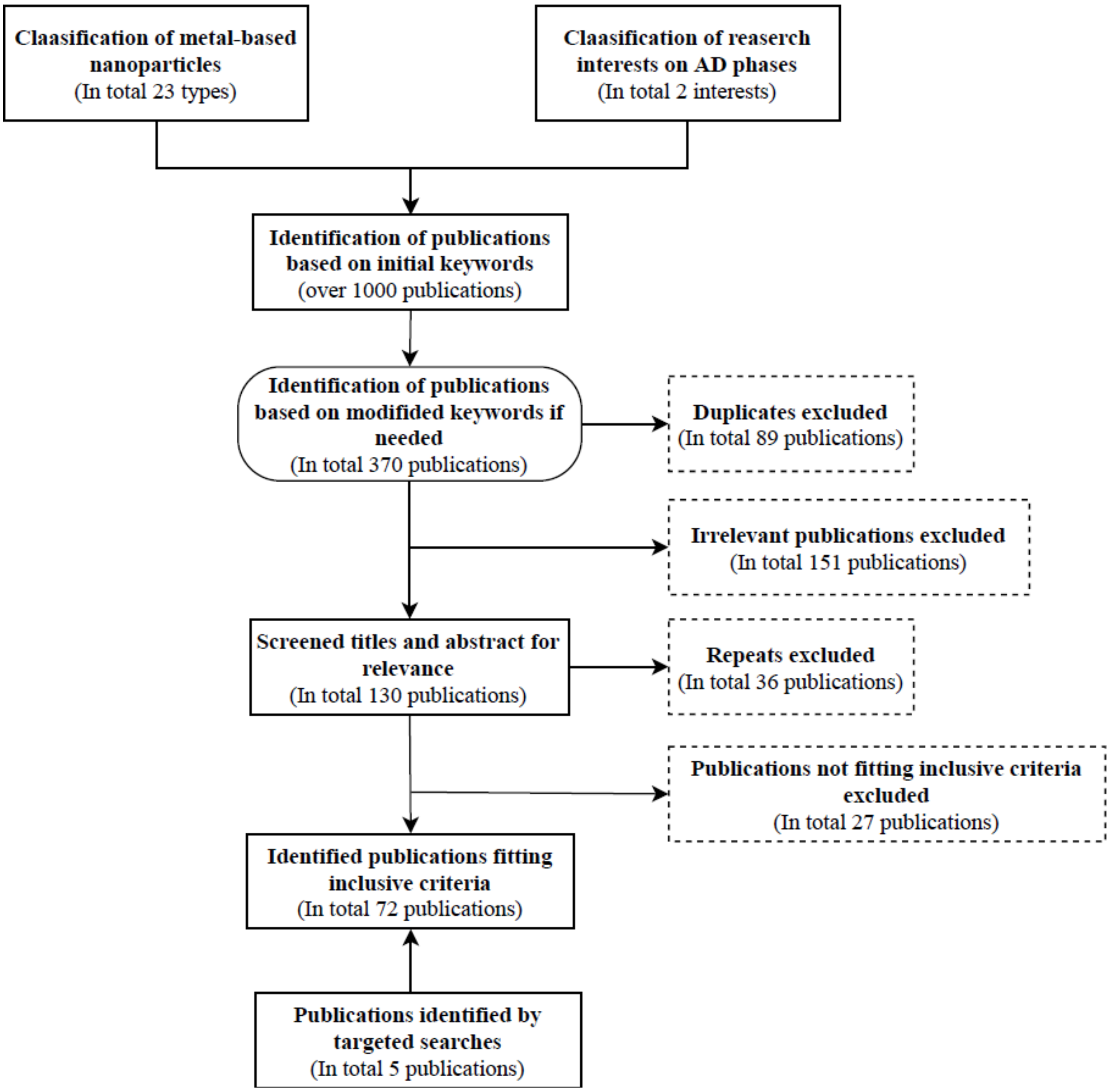

Fig. 2. The process of literature searches of this review.

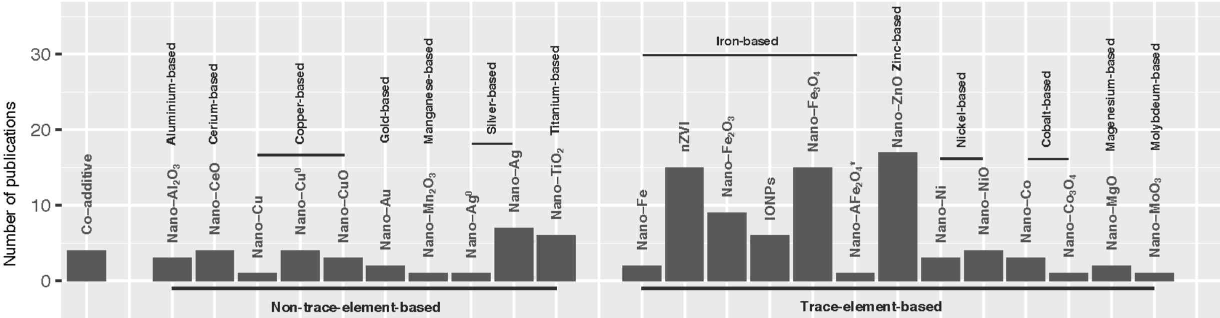

Fig. 3. Categorization and counts of publications in this study.

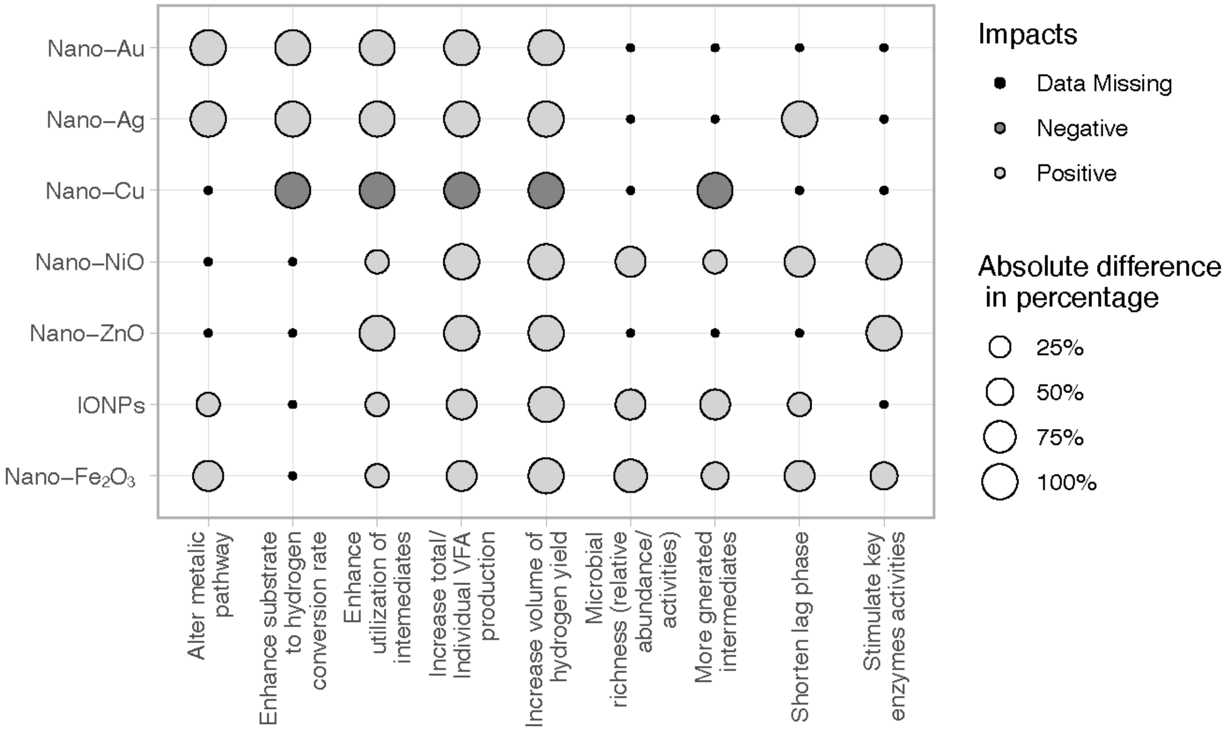

Fig. 4. Qualitative analysis for metallic nanoparticles impact on AD fermentation phase.

*: Only one publication was included in this review.

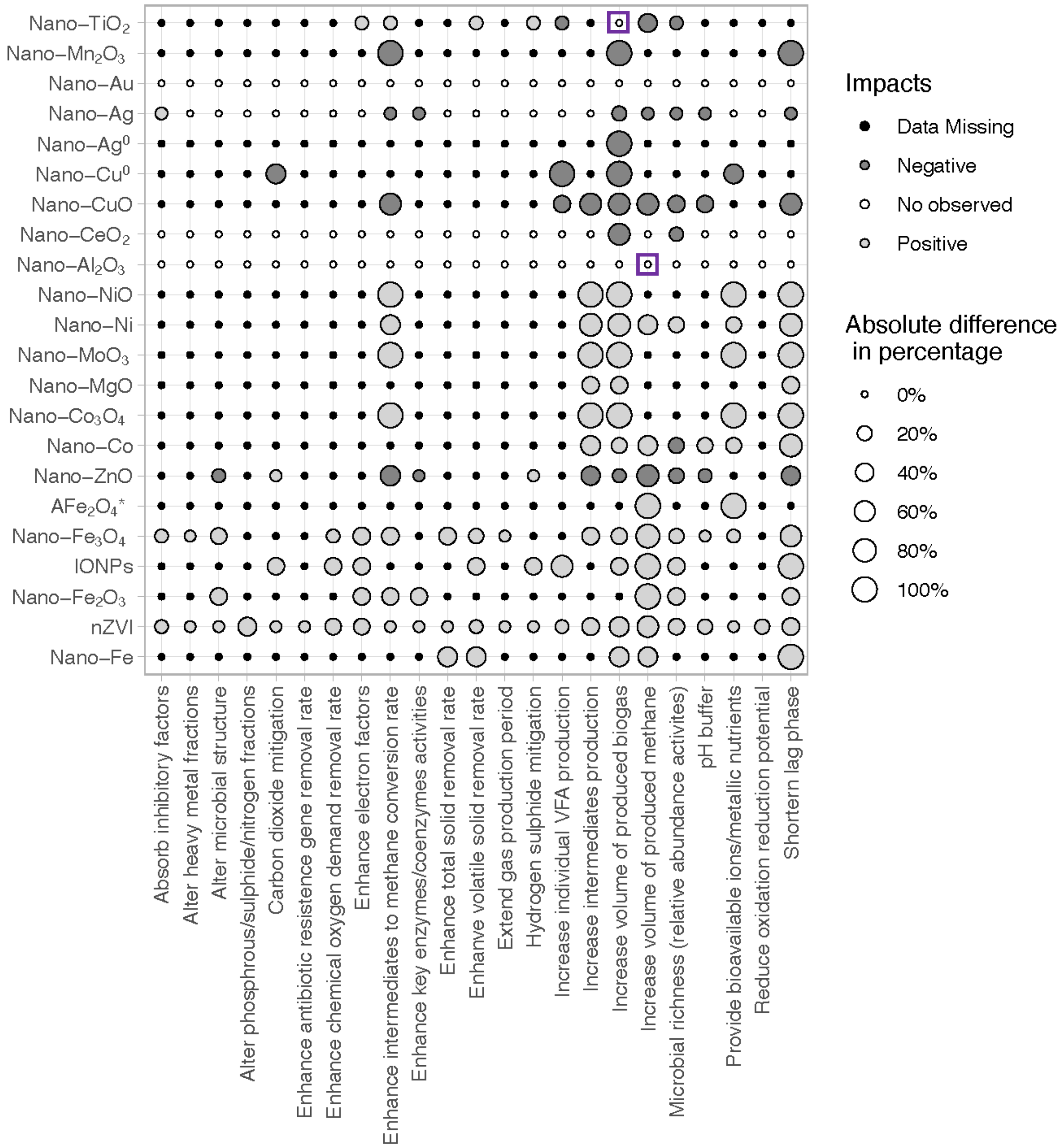

Fig. 5. Qualitative analysis of metallic nanoparticles impact on methane-production and overall AD processes.

*: A stands for a types of metal, such as nickel and zinc.

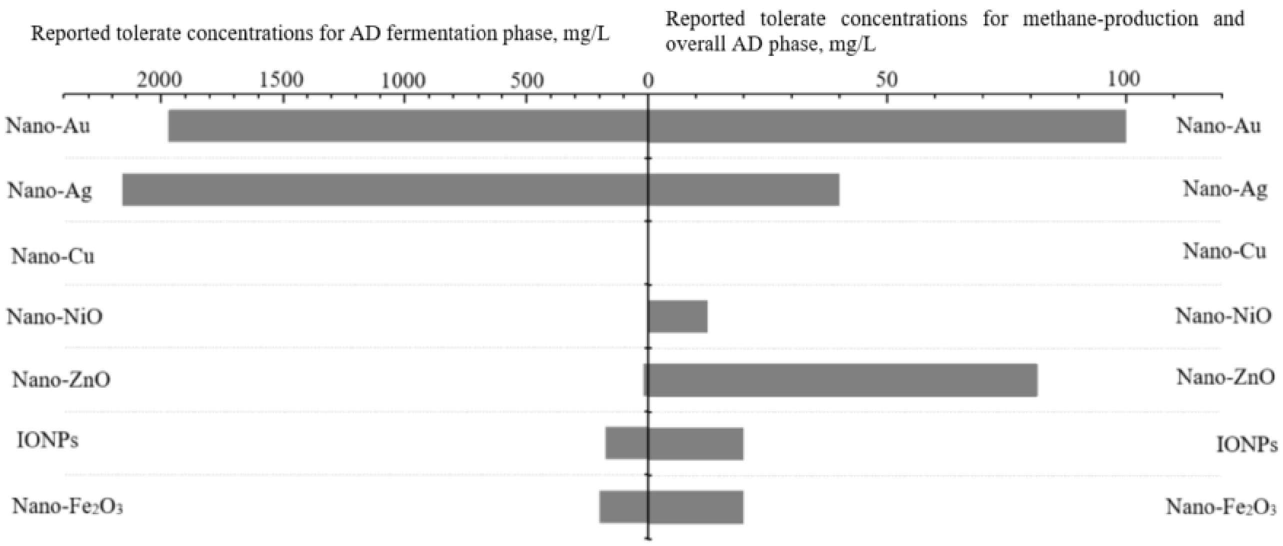

Fig. 6. Comparison of reported tolerate concentrations of metallic nanoparticles for both research interests.

Tables

Impact of Metallic Nanoparticles on Anaerobic Digestion: a Systematic Review

Table 1. Reported tolerate concentrations of selected metallic nanoparticles on the AD fermentation phase.

Types of nanoparticles	Size of the nanoparticles, nm	Highest reported concentrations	Notes	Reference
Nano-Fe_2O_3	33, ~50[a] and <100	200 mg/L	Best performance	(Gadhe et al., 2015), (Han et al., 2011)
IONPs	~50	175 mg/L	Best performance	(Mohanraj and Kodhaiyolii, 2014), (Mohanraj et al., 2014)[b]
Nano-ZnO	<100	10 mg/g VS	No adverse impacts	(Elreedy et al., 2019)
Nano-NiO	23	5 mg/L	No adverse impacts	(Gadhe et al., 2015)
Nano-Cu	~100[a]	0 mg/L[c]	Inhibit AD fermentation	(Mohanraj et al., 2016)
Nano-Ag	~15[a]	20 nM	Best performance	(Zhao et al., 2013)
Nano-Au	5	10 nM	Best performance	(Zhang and Shen, 2007)

[a]: Approximate.

[b]: The reason for choosing this concentration as up limit is due to the selection of feedstock (two studies applied with similar selection) and size range of the nanoparticle (similar choice with the selection of nano-Fe_2O_3).

[c]: The presence of this nanoparticle inhibit the AD fermentation phase.

Table 2. Reported tolerate concentrations of selected metallic nanoparticles on the methane-production stage and overall AD process.

Types of nanoparticles	Size of the nanoparticles, nm	Highest reported concentrations	Notes	Reference
Nano-Fe	~10[a]	20 mg/L	Best performance	(Abdelsalam et al., 2016a)
nZVI	100	0.5 g/g VS	Best performance	(Pan et al., 2019)
Nano-Fe_2O_3	<30	100 mg/g TSS	Best performance	(Wang et al., 2016)
IONPs	~50[a]	20 mg/L	Best performance	(Sreekanth and Sahu, 2015)
Nano-Fe_3O_4	~10[a]	100 mg/L	Best performance	(Arbiol et al., 2014)
Nano-AFe_2NiO_4	~50[a]	400 mg/L	Only one publication	(Lin et al., 2018)
Nano-ZnO	~30[a]	1 mM	Limited adverse impacts	(Zhu et al., n.d.)
Nano-Co	~30[a]	1 mg/L	Best performance	(Abdelsalam et al., 2016b)
Nano-Co_3O_4	~30[a]	12.5 mg/L	Only one publication	(Juntupally et al., 2017)
Nano-MgO	<100[b]	1 mg/L TSS[b]	No adverse impacts	(Wang et al., 2016)
Nano-MoO_3	15	12.5 mg/L	Only one publication	(Juntupally et al., 2017)
Nano-Ni	~20[a]	2 mg/L	Best performance	(Abdelsalam et al., 2016b)
Nano-NiO	~20[a]	12.5 mg/L	Only one publication	(Juntupally et al., 2017)
Nano-Al_2O_3	<50	1500 mg/L	Limited adverse impacts	(Gonzalez-Estrella et al., 2013)
Nano-CeO_2	~10[a]	0.16 mg/mL	Limited adverse impacts	(García et al., 2012)
Nano-CuO	30	15 mg/L	Limited adverse impacts	(Luna-delRisco et al., 2011)
Nano-Cu^0	~50[a]	0.382 mM Cu	Limited adverse impacts	(Gonzalez-Estrella et al., 2016, 2015b)
Nano-Ag^0	<100	1500 mg/L	Only one publication	(Gonzalez-Estrella et al., 2013)
Nano-Ag	~20[a]	40 mg/L	Limited adverse impacts	(Yang et al., 2012a)
Nano-Au	~20[a]	0.10 mg/mL	Only one publication	(García et al., 2012)
Nano-Mn_2O_3	<100	1500 mg/L	Only one publication	(Gonzalez-Estrella et al., 2013)
Nano-TiO_2	25	500 mg/L	Best performance	(Farghali et al., 2019)

[a]: Approximately.

[b]: Total suspended solids.