

Enhanced performances of anaerobic digestion processes treating organic wastes: Role of iron and carbon based nanomaterials

Hongbo Liu, Jian Wen, Qiting Liu, Runshan Li, Eric Lichtfouse, Claudia Maurer, Jingjing Huang

▶ To cite this version:

Hongbo Liu, Jian Wen, Qiting Liu, Runshan Li, Eric Lichtfouse, et al.. Enhanced performances of anaerobic digestion processes treating organic wastes: Role of iron and carbon based nanomaterials. Surfaces and Interfaces, 2023, 43, pp.103548. 10.1016/j.surfin.2023.103548 . hal-04271322

HAL Id: hal-04271322 https://hal.science/hal-04271322

Submitted on 6 Nov 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés. https://doi.org/10.1016/j.surfin.2023.103548

Enhanced performances of anaerobic digestion processes treating organic wastes: Role of iron and carbon based nanomaterials

Hongbo Liu^{a,*}, Jian Wen^a, Qiting Liu^a, Runshan Li^a, Eric Lichtfouse^{b,c}, Claudia Maurer^{d,*}, Jingjing Huang^d

^a School of Environment and Architecture, University of Shanghai for Science and Technology, 516 Jungong Road, Shanghai, 200093, China

^b State Key Laboratory of Multiphase Flow in Power Engineering, International Research Center for Renewable Energy, Xi'an Jiaotong University Xi'an, Shaanxi, 710049,

China

^c Aix-Marseille University, CNRS, IRD, INRAE, CEREGE, Aix en Provence 131000, France

^d University of Stuttgart–Institute of Sanitary Engineering, Water Quality and Waste Management, Bandtale 2, 70569 Stuttgart, Germany

ARTICLE INFO

Keywords: Organic waste Anaerobic digestion Frequently-used nanomaterials Performance improvement Antibiotic resistance gene

ABSTRACT

Issues of climate change, energy demand and antibiotic resistance are calling for advanced methods to convert waste into fuels, value-added materials and safe byproducts. Anaerobic digestion (AD) is a major technology treating organic-rich wastes such as sewage sludge, kitchen waste, and animal manure. AD allows to convert waste into energy such as biogas and electricity, and resources such as fertilizers. Nevertheless, biogas production from organic waste is limited by the low biodegradability of resistant organic matter and the short retention time in AD bioreactors. As a consequence, recent researches have focused on the use of additives to improve the performance of AD. For example, nanomaterials are increasingly used as additives due to their properties in the promotion of direct inter-species electron transfer between microorganisms, and the improvement of the microbial community structure. In this study, we review firstly the contribution of nanomaterials to system stability, digestive performance and risk control of AD processes systematically. Then we sorted the enhanced performances by co-digestion of nano-magnetite with sewage sludge, kitchen waste, livestock and poultry manure thoroughly. Finally we discussed mechanisms on how nanomaterials such as iron- and carbon-based nanomaterials addition could enhance production of volatile fatty acids, and inhibit the production of hydrogen sulfide and the transmission of antibiotic resistance genes simultaneously.

1. Introduction

The global energy crisis and climate change are urgently calling for the development of sustainable energy systems since renewable energy sources can prevent resource depletion, ecological degradation, and global warming effectively [1]. The rise of the economy and living standards in many countries is also increasing the production of organic waste. The World bank projected increasing waste generation all over the world. In many cases, the organic waste is landfilled where the energy and nutrients in the organic waste is basically wasted [2]. There are many kinds of solid organic waste, including sewage sludge, kitchen waste, human and animal manure, green plant waste and agricultural waste, mainly containing biodegradable organic components with a water content of 85–90 % [3]. Therefore, organic wastes are a potential source of energy and value-added materials that should be recovered

during waste treatments [4]. For that, many researches are actually focusing on improving anaerobic digestion (AD), a key biological waste treatment technology.

Anaerobic digestion is a complex dynamic system involving microbial, biochemical, and physicochemical processes, with multiple biochemical metabolic pathways [5]. As shown in Fig. 1, AD usually proceeds in four steps: hydrolysis, acidogenesis, acetogenesis, and methanogenesis [6]. In the absence of oxygen, anaerobic bacteria ferment biodegradable substances into methane and convert the organic waste into biomass energy. At the same time, minerals such as ammonium salts, phosphates and sulfides are retained in the digestate, which can be further used to produce soil conditioners [7] and organic fertilizers [8]. During this process, anaerobic microorganisms produce methane by breaking down organic matter. However, the purity (volume content) of methane produced by AD is usually between 50 % and

* Corresponding authors. E-mail addresses: Liuhb@usst.edu.cn (H. Liu), claudia.maurer@iswa.uni-stuttgart.de (C. Maurer).

70 % [9]. As shown in Fig. 1, other major impurity gases include hydrogen sulfide (H₂S), gaseous free ammonia (NH₃), carbon dioxide (CO₂), and hydrogen (H₂). These gases are mainly produced by microbial metabolism during AD, where CO₂, H₂, NH₃ and H₂S play different roles. CO₂ and H₂ are common gases produced during AD and play an important role in the system. In addition, H₂ is an important raw material for methane productionan with CO₂ [10]. H₂S and NH₃ are mainly produced by sulfate-reducing bacteria and ammonia-oxidizing bacteria. H₂S can be generated together with methane, but at high concentrations, it can also have a toxic effect. Ammonia nitrogen concentration higher than 1500 mg/L will inhibit AD and affect the metabolism and digestion process of microorganisms. Managing free ammonia content in bulk water is one of the important tasks for AD processes [11].

Researchers are currently attempting to upgrade technologies to achieve better biogas yield and higher methane content, as well as maximize energy recovery and minimize environmental impact, e.g. by adding nanomaterials [12].

Nanomaterials have unique thermal, mechanical, structural, and physicochemical properties such as size, specific surface area, surface structure, solubility, and catalysis, and therefore have a wide range of applications [13]. Nanomaterials applied in AD are mainly because of their properties such as higher specific surface area. Suanon et al. applied nano-zero-valent iron (nZVI) and commercial iron powder to the AD of municipal sludge, and found that the Brunauer-Emmett-Teller surface area of nZVI (23.3 m²/g) is about 10 times that of commercial iron powder (2.48 m²/g), but the dosage of nZVI is only one-tenth of that of the commercial iron powder [14]. The larger surface area increases the contact between wastes and microorganisms. Various carbon-based nanomaterials are able to enhance the electron exchange between bacteria and methanogens attached to the surface of biochar due to the presence of specific surface functional groups [15].

Nanomaterials have remarkable properties due to their very small

size, diverse morphology, high reactivity, and chemical stability [16]. As a consequence, nanomaterials can interact with the digestion matrix and microorganisms in AD systems to enhance bacterial activity and process performances efficiently [17,18]. In this study, we review the literature on the role of nanomaterials in improving biogas production, focusing on maintaining system stability, suppressing NH₃ and H₂S production, improving electron transfer within microbial communities, and extracellular polymer production. We also present the use of nanomaterials to inactivate antibiotic resistance genes that occur in wastewater.

1.1. Performances and maintainance of the nanomaterials enhanced AD processes

Literature was reviewed to describe the nanomaterials focused on iron-based and carbon-based nanomaterials. To identify papers for the literature review, we reviewed approximately 400 papers on nanomaterials for enhanced AD, and we performed keyword co-occurrence analysis using VOS viewer. The results are shown in Fig. 2. Each keyword is presented in the form of nodes, and the size of the nodes indicates the importance of the keyword. At the same time, the connection between nodes indicates the co-occurrence relationship between these keywords, and the thickness of the connection indicates the strength of the co-occurrence. We count keywords that appear more than 5 times. Of the 2195 keywords, 233 meet the threshold.

Among the keywords that co-occurred more than five times, we found that nZVI, activated carbon, biochar, graphene, magnetite nanoparticles (nFe₃O₄), and carbon nanotubes appeared 63, 35, 33, 9, 8, and 6 times, respectively. Results show that most current research is focused on iron-based nanomaterials and carbon-based nanomaterials. This phenomenon may be related to the properties of these two materials. Also, iron- and carbon-based nanomaterials are readily available as raw materials and can be easily recycled for secondary use. This underlined

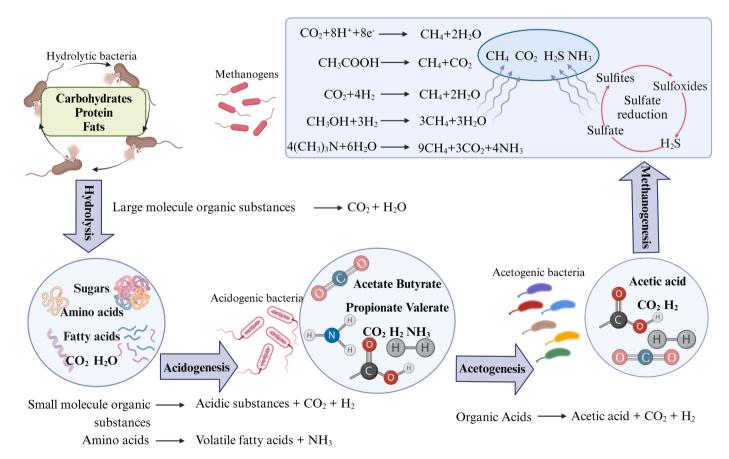


Fig. 1. Diagram of anaerobic digestion and main biogas generation nodes. Created with BioRender.com. Publication license has been obtained.

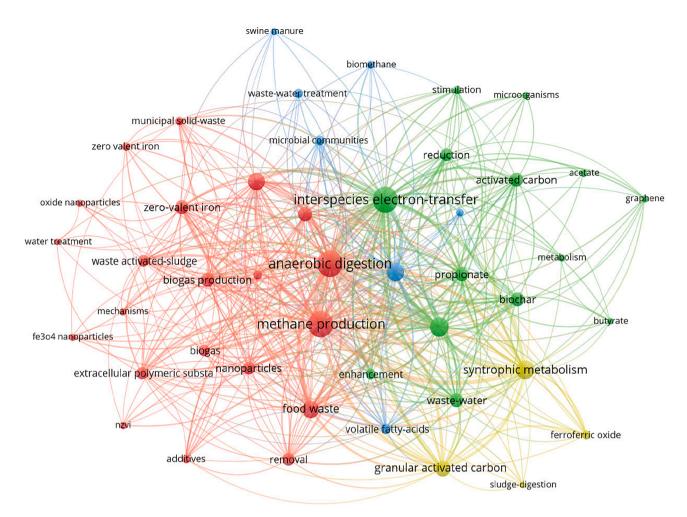


Fig. 2. Keywords co-occurrence network analysis using VOS viewer software. Keyword co-occurrence analysis based on nanomaterials, enhancement effects and anaerobic digestion were conducted based on 400 articles published in journals through the Web of Science Network.

the focus on these materials.

Here, we explain specifically how these properties enhance biogas production, maintain system stability, and suppress NH_3 and H_2S production. Based on literature review, the properties of iron-based and carbon-based nanomaterials and their effects on methanogenesis by AD are summarized in Table 1.

1.1.1. Enhancement of AD performances by dosage of nanomaterials

Biogas yield and methane content are major indicators of AD performance. After 80 days of digestion, the cumulative maximum biogas production increased by 15.7 % and 13.4 % respectively compared with the control group [19]. And the biogas composition analysis showed that the nano-iron also increased the methane content in the biogas by up to 17.2 %. The main reason for the increase in methane production is that the nano-iron formed micro-electrolysis units in AD reactors to decompose the sludge matrix. The total polysaccharide degradation rate increased by 29.6 % after dosing nZVI, and the iron involved micro-electrolysis units can promote the hydrolysis and acidogenesis efficiencies. Kassab et al. investigated the effect of nFe₃O₄ on the hydrolysis and acidogenesis stage of AD, and found that after adding nFe₃O₄, the methane production increased by 50.8 % after 25 days of digestion, while the soluble COD content of the system increased significantly [20]. The hydrolysis rate can be increased by 30.0 % to 40.0 % and the acidification rate by 44.0 %, while the amount of acetic acid produced by the system is directly related to the amount of nFe₃O₄ added.

Studies have pointed out that the optimal dosage of nFe₃O₄ can

stimulate the growth of microorganisms, especially the methanogens in the AD system. Due to the existence of magnetite, the ability of direct interspecies electron transfer (DIET) between species is greatly enhanced. The addition of nFe_3O_4 can improve the relationship between the syntrophic bacteria *Geobacter* and *Methanosarcina*. Through the electron channel formed by nFe_3O_4 , the electrons generated by *Geobacter* are directly transferred to *Methanosarcina* [21]. In addition, nFe_3O_4 particles may be attached to the cell membrane of methanogens, acting as electron shuttles and promoting intracellular electron transfer [22].

Studies have shown that the type of fermentation is closely related to the oxidation-reduction potential (ORP) value. As a strong reducing agent, nZVI can reduce the ORP value and create good conditions for acetic acid fermentation [23]. However, hu et al. found that hydrogenotrophic methanogenesis contributed more to the methanogenesis process in the system with added nZVI. In the AD reactor with nZVI dosage, the oxidation and acidification process of iron can produce H₂. H_2 is an impurity component in biogas. As shown in Fig. 1, during the methanogenesis process, hydrogenotrophic methanogens can use H₂ as an electron donor to reduce CO₂ to produce methane. Therefore, the H₂ produced by nZVI can be used by hydrogenotrophic methanogens to indirectly promote the formation of methane [24]. At the same time, compared with not adding nZVI, adding 1.0 g/6.0 g dry matter nZVI can increase the methane content by 37.4 %. During this period, it was observed that the CO2 content was also reduced by nearly 80 %, and H2 was fully utilized. Even though the hydrogenotrophic methanogenesis is greatly enhanced and contributes more to the methanogenesis process,

Table 1

Impact of common nanomaterials based on the performance of anaerobic digestions. nZVI: nano zero-valent iron. nFe₃O₄: Fe₃O₄ nanomaterials, rGO-MNPs: reduced graphene oxide materials modified with magnetite nanomaterials.

Type of Nanomaterials	Substrate/ Type of Biochar	Size/ Dosage	Operating Cycle	Digestion Temperature	Biogas Production /Methane Content Increase Rate	Refs.
nZVI	Anaerobic activated sludge	Less than 100 nm	14 days	37±3 °C	25.23 % (biogas) 31.38 % (methane)	[41]
nZVI	Activated sludge	0.25 g/L 20–100 nm 0.50–1.0 g/L	17–80 days	35–37 °C	15.70–30.40 % (biogas) 8.75–40.40 % (methane)	[19] [23] [42]
nZVI	Glucose	100 nm	20 days	37 °C	23.90 % (biogas)	[43] [44]
nZVI	Food waste	5.0 g/L 40–600 nm 5.0 g/L	15–65 days	35–37 °C	8.50-62.58 % (biogas)	[45] [46]
nZVI	Manure	9–80.9 nm 0.20–0.1 g/L	50-69 days	35–37 °C	29.10-45 % (biogas)	[40] [47] [48]
nFe ₃ O ₄	Dewatered and secondary sludge	20 nm 1.0 g/L	80 days	35±2 °C	13.44 % (biogas) About 10 % (methane)	[19]
nFe ₃ O ₄	Activated sludge	12–30 nm 0.05–0.25 g/L	13–25 days	35–37 °C	60–70 % (biogas) 13.20–50.80 % (methane)	[49] [50] [20]
nFe ₃ O ₄	Canola straw and banana plant waste Buffalo dung and banana plant waste	1 μm 2.025 mg /L 1 μm	40 days	37±1 °C	39.40 % (methane) 33.10 % (methane)	[51]
nFe ₃ O ₄	Manure/Chicken, cattle dung and poultry litter	1.25 mg /L 4.2–400 nm 0.15–0.20 mg/ L	50–80 days	35–37 °C	27.50–66 % (biogas)	[22] [52] [47] [48]
nFe ₃ O ₄	Food waste	300–600 nm 5.0 g/L	65 days	37±1 °C	6.00 % (biogas)	[45]
Biochar	Activated sludge/Corn stover, biogas residue, blue algae and coconut shell	0.064–0.12 g/g dry matter	34–35 days	35–55 °C	9.66–39.11 % (biogas) 30.64–46.16 % (methane)	[25] [31] [27]
Biochar	Excess sludge/ Fruitwood	1.0 g/g dry matter	45 days	37 °C	27.80 % (biogas)	[33]
Biochar	Manure/ Residues biochar, wheat straw, Fruitwood and Chicken manure biochar	0.05–0.058 g/g dry matter	60–72 days	35–37 °C	6.97–68.90 % (biogas)	[26] [32] [53]
Biochar	Sorghum/Rice husk	0.5 g/g dry matter	25 days	35 °C	25 % (biogas)	[30]
Biochar	Food waste/Wood chips and biogas residue	0.04–0.08 g/g dry matter	27 days	37–55 °C	10.50-18 % (biogas)	[54] [55]
Biochar	Food waste/ Sludge-derived and wood pellets	0.83–1.06 g/g dry matter	11–46 days	35 °C	214–474 % (biogas)	[56] [57]
nZVI- biochar	Waste activated sludge/Corn stover-derived	59.2 nm 0.21 g/g dry matter	34 days	37±1 °C	29.56 % (methane) 115.39 % (biogas)	[25]
Magnetic biochar	Municipal solid waste/Magnetic rice-straw	25.66 nm 0.5 %, w/w	25 days	35 °C	11.70 % (biogas)	[35]
Magnetic biochar	Artificial dairy wastewater/ Magnetite-contained	Particular amounts	last 8 days	37 °C	38.10 % (biogas)	[36]
Nano-graphene	Anaerobic sludge	0.8–1.2 nm 30 mg/L	55 days	$20\pm210\pm2~^\circ\text{C}$	14.30 % (biogas)	[39]
rGO-MNPs	Anaerobic sludge	8.3 ± 3.6 nm 50 mg/L	16 days	37 °C	47.00 % (biogas)	[40]

the acetoclastic methanogenesis process is also enhanced. Zhang et al. conducted a series of experiments using nZVI-loaded biochar (nZVI-BC) to enhance AD performances, and found that 0.21 g/g dry matter nZVI-BC can significantly increase the production of total volatile fatty acids (VFAs) and improve VFAs composition, optimize thermodynamic conditions, inhibit propionic acid fermentation, and promote methane production [25]. From the analysis of microbial results, the abundance of *Methanosaeta* dropped from 63.4 % without dry nZVI-BC dosage to 55.93 % of 0.21 g/g dry matter nZVI-BC dosage. The abundance of two hydrogenotrophic methanogens, *Methanobacterium* and *Methanospirillum*, was higher than that of the control group, which implied that the addition of nZVI-BC could change the abundance of systemic archaea and increase the diversity of microbial communities. Therefore, a certain dosage of nZVI-BC can improve the hydrogenotrophic methanogenesis reaction and increase methane production.

Patel et al. used cattle manure as feedstock and dosed biochar at 0-14 mg/L into the reactor; all concentrations of biochar were found to increase the methane content of the AD system [26]. Compared with no added biochar, the methane content was 35.2 % higher in the manure added with 10 mg/L biochar. This is because biochar promotes direct electron or hydrogen transfer between microorganisms, improving the activity of microorganisms.

Liu et al. compared the effects of biochars from biogas residues, coconut shells and corns on the anaerobic co-digestion process [27]. The results showed that the daily mean methane production increased by 46.2 %, 27.7 % and 30.6 % with the addition of the three biochars, respectively, compared with the control group. After the dosage of biochars, the fluorescence intensity of protein and cellulose in the system decreased significantly, indicating that biochar can accelerate the hydrolysis process of protein and ligno-cellular matter and promote AD

performances. The abundance of *Methanobacterium* and *Methanobacter*, which are considered to enhance hydrogenotrophic methanogenesis, increased by 2 times and 4 times after the addition of residue biochar respectively [28]. The unique alkaline properties of biochar can enhance the process of hydrogenotrophic methanogenesis. Increased methane production rates are accompanied by slower pH drops because biochar can alleviate the acid inhibition caused by VFAs produced by hydrolytic acidification [29]. Biochar can also increase the conversion rate of microorganisms to VFAs [30].

Jiang et al. found that the addition of blue algae biochar can significantly improve the microbial community structure and greatly increase the abundance of *Methanoscrina* species during the AD of sludge hydrolyzate [31]. Under low inoculum, the rate of VFAs consumption slows down significantly, and the *Methanoscrina* receives additional electrons through cyanobacterial biochar-mediated DIET to enhance AD performances. Pan et al. confirmed that high specific surface area and porous biochar can promote DIET, enabling methanogens such as *Methanosarcina* to establish specialized methanogenic regions [32].

Yan et al. found that when the TS of inoculated sludge was 10 g and the waste apple branch biochar with a sludge concentration of 100 % TS was added, the abundance of methanogens 45 days after AD was 105.4 % higher than before digestion, where The abundance of hydrogenotrophic methanogens such as methane microorganisms is 59.7 % [33,34]. When the added TS of inoculated sludge was 20 g, the concentration of methanogens was found to be approximately 20.6 % higher than the previous group, and the abundance of methane microorganisms increased to 64.1 %. Therefore, biochar can significantly increase the number of Methanomicrobiales and improve hydrogenotrophic methanogenesis.

Qin et al. dosed synthetic magnetic biochar into an AD reactor and found that a large number of microorganisms with hydrolysis, acido-/ acetogen production and methanogenic ability were adsorbed on the magnetic biochar, which can significantly shorten the contact distance of microorganisms [35]. The Moraxellaceae and Pseudomonadaceae, two strains that can participate in DIET, were also detected on the magnetic biochar. M., Wang et al. also confirmed that magnetic biochar with high conductivity can act as an electron shuttle in syntrophic metabolisms in the digestive system, improving the AD performance significantly [36]. Studies have shown that, on the one hand, as the pyrolysis temperature increases, the formation of magnetite increases, so the dissimilatory iron reduction induced by amorphous iron oxide is weakened, and more terminal electrons are used for methane production [36,37]. On the other hand, magnetite can act as an electron conduit to stimulate DIET between syntrophic bacteria and methanogens [38]. Therefore, biochar can significantly increase the number of Methanomicrobiales and improve hydrogenotrophic methanogenesis.

Tian et al. applied 30 mg/L nano-graphene to an up-flow anaerobic sludge bed. After 55 days of AD, methane production increased by 14.3 % compared with the control group [39]. Here, the presence of graphene nanomaterials accelerated the cleavage of acetic acid and enhanced the acetoclastic methanogenesis. Covarrubias-García et al. increased methane production by 47.0 % with the addition of reduced graphene oxide materials modified with magnetite nanoparticles (rGO-MNPs) [40]. The application of this composite nanomaterial increased the electron shuttling capacity and the hydrogenotrophic activity of the microorganisms, while iron ions released from the system acted as nutrients for microbial growth. Overall, the addition of nanomaterials induces a major improvement in biogas production and purity, with the best improvement observed for iron-based composite nanomaterials.

In particular, nanomaterials can optimize the two so-called impurity gases, H_2 and CO_2 , and convert them into methane by promoting hydrogenotrophic methanogenesis, and to increase the methane content in the biogas. In short, due to their larger specific surface area and higher reactivity, nanomaterials can participate in reactions as catalysts, microbial supports, electrode catalysts, and mass transfer enhancers, thereby improving reaction rates, product selectivity, and stability. It

can also be concluded from Table 1 that the effect of iron-based and carbon-based nanomaterials on AD is also limited by the effect of the digested substrate. The specific summary is as follows:

Firstly:0.5–1.0 g/L nZVI, 0.05–0.25 g/L nFe₃O₄, 0.1 g/g dry matter biogas residue and corn straw biochar are suitable for treating sewage sludge.

Secondly:5.0 g/L nZVI, 5.0 g/L nFe $_{3}O_{4},$ and 1.0 g/g dry matter biogas residue and sawdust biochar are suitable for treating kitchen waste.

Finally:20–100 mg/L nZVI, 15–20 mg/L nFe $_3O_4$ and 0.05 g/g dry matter fruit wood biochar are suitable for treating livestock and poultry manure.

In addition to the above, the potential of iron-modified biochar nanomaterials for AD is also huge. In the future, research can focus on the mechanism and application of iron-modified biochar in AD.

We performed a simple overall cost analysis of adding nanomaterials to AD. As shown in Table 2, the overall cost is determined by the production cost of the nanomaterial itself and the economic benefits of the methane generated by the nanomaterial. Without considering transportation costs, the price of biochar is approximately 2.43 Yuan/Kg [58]. Since there are few literatures mentioning the manufacturing cost of nFe₃O₄, we start from the raw materials, especially nFe₃O₄ is mostly synthesized by co-precipitation of ferric chloride and ferrous sulfate. Their costs are 3 Yuan/kg and 0.22 Yuan/kg respectively, so the cost of 1 Kg of nFe₃O₄ is about 7.25 Yuan. In addition, nZVI can be synthesized through the chemical reduction method of ferric chloride and sodium borohydride. However, since the commercial price of sodium borohydride is about 60 times that of ferric chloride, the cost of 1 kg of nZVI is approximately 428.88 yuan. In addition, the price of generated methane is based on the average natural gas price for residential users of 3.91 Yuan/m³ [59]. Based on the above information, without considering other factors (excipients, energy consumption, etc.) in the production process of nanomaterials, we conducted a rough cost analysis of several typical documents cited in Table 1 based on 1t substrate. If the economic output from additional methane produced is greater than the costs of the nanomaterials, the overall cost effectiveness is displayed as positive, otherwise it is negative. From Table 2, we can see that nFe₃O₄ performs relatively well, probably because its dosage is low but its economic output is high. However, when it comes to kitchen organic waste, it is difficult to achieve good economic results with high dosages. Unless magnetic separation of nFe₃O₄ is used for recycling. In addition, it can be seen from the table that anaerobic co-digestion is also an important means to recover costs [57]. Overall, the application of iron-based and carbon-based nanomaterials can bring cost advantages in terms of increasing gas production rates, reducing gas treatment costs, and improving system stability, making AD a more attractive option for waste disposal and energy recovery methods. However, there are still relatively few applications in actual engineering, and sufficient engineering design and economic evaluation need to be carried out according to specific circumstances to ensure that the advantages of these nanomaterials are maximized.

1.1.2. Maintainance of the nanomaterials enhanced AD system

Ammonia nitrogen is an essential nutrient for anaerobic microorganisms during AD processes; at certain concentrations, ammonia nitrogen provides a good buffering effect on the digestion process. However, excessive concentrations of ammonia nitrogen could also inhibit the growth of microorganisms. The two main forms of ammonia nitrogen are ionized ammonium (NH⁴₄) and gaseous free ammonia (NH₃). In general, NH₃ is permeable to bacterial cells, so it is more toxic than NH⁴₄ [60]. In the AD process, ammonia is produced mainly from two pathways: ammonia dissociation and anammox reaction. During the AD treatment, organic matter is decomposed by anaerobic bacteria into small molecular compounds, including proteins and amino acids containing amino groups (-NH₂). These organic compounds were decomposed under anaerobic conditions, producing substances such as NH₃

Table 2	
Overall cost analysis of AD with additional nanomaterials.	

Type of Nanomaterials	Dosage	Digestive Substrate	Additional Average Methane Production	Economic Output from Additional Methane Produced (¥)	Costs of the Nanomaterials (¥)	Overall Cost Effectiveness
nZVI	1.0 g/L	Sewage sludge	20.58 ml/g VS	1.07	428.88	Negative
nZVI	5.0 g/L	Kitchen waste	36.4 ml/g VS	24.73	2129.4	Negative
nZVI	0.1 g/L	Livestock and poultry manure	78 ml/g VS	201.89	42.888	Positive
nFe ₃ O ₄	120 mg/L	Sewage sludge	112 ml/g VS	10.22	0.806	Positive
nFe ₃ O ₄	5.0 g/L	kitchen waste	29 ml/g VS	19.70	36.25	Negative
nFe ₃ O ₄	20 mg/L	Livestock and poultry manure	53.13 ml/g VS	97.3	0.145	Positive
Biogas residue biochar	0.16 g/g dry matter	Sewage sludge and kitchen waste	136.5 ml/g VS	26.88	19.44	Positive
Corn straw biochar	0.058 g/g dry matter	Sewage sludge	20.84 ml/g VS	4.84	14.094	Negative
Biogas residue biochar	1.0 g/g dry matter	Kitchen waste	32.3 ml/g VS	6.31	14.58	Negative
Sawdust biochar		Kitchen waste and sewage sludge	171.1 ml/g VS	144	60.75	Positive
Fruit wood biochar	0.05 g/g dry matter	Livestock and poultry manure	120 ml/g VS	90.18	33.92	Positive

and some organic acids. Furthermore, the decomposition and transformation of some intermediate products such as amino compounds will generate NH₃.

Jia et al. added 1000 mg/L nZVI to the AD of sludge and found that the concentration of ammonia nitrogen can be maintained at 600-800 mg/L during the stable period [42]. Compared with the control group, the dosage of 1000 mg/L nZVI reduced the concentration of ammonia nitrogen and created the most favorable conditions for biogas production. Here, nZVI acts as a pH buffer through the dissociation of Fe⁰ and Fe^{3+} , thus reducing the ammonia nitrogen content and promoting methane production [9]. Amen et al. also found that adding nZVI can remove 18.6 % more total ammonia nitrogen than the control group because nZVI can remove ammonia nitrogen through cation exchange [61]. Zero valent iron was shown to activate the methanogenic activity of Methanosarcina in a manner that enhanced electron conversion under ammonia-suppressed conditions. Methanosarcina is capable of acetoclastic methanogenesis and hydrogenotrophic methanogenesis, and can directly accept electrons to produce methane through DIET [62]. Zhang et al. found that compared with the control group, under the condition of high ammonia nitrogen concentration, the biogas production after adding nZVI and sulfurized nZVI was still 10 %-60 % higher [63]. The two materials showed the best promoting effect at 1500 and 2500 mg/L ammonia nitrogen concentration, indicating that these two materials can improve the tolerance of the system to ammonia nitrogen and relieve the high inhibitory effect caused by ammonia nitrogen stress. However, when the sulfidated nZVI was added, the abundance of the previously mentioned Methanosarcina increased by nearly 3 times, indicating that sulfidated nZVI can enhance methanogenesis through DIET [32].

Sharma et al. proposed that biochar has a good ammonia reduction effect, which is attributed to the adsorption of ammonia ions in the matrix by biochar [64]. W., Yan et al. found that under the conditions of ammonia nitrogen of 1500.0 mg N/L and free ammonia of 49.9 ± 3.9 mg NH₃—N/L, the time to peak VFAs concentration is prolonged and VFAs accumulation is higher [65]. In all experimental groups, the methane production rate decreased significantly, and the intracellular adenosine triphosphate concentration decreased by 25 to 55 %. This indicates that microbial metabolism is inhibited. Although the AD performance was inhibited, the addition of carbon nanotubes could promote the rapid recovery of methanogenic activity. Iron-modified biochar also exhibited excellent adsorption capacity. Deng et al. successfully increased the ammonia nitrogen adsorption capacity of pure corncob biochar from 5.0 mg/g to 6.4 mg/g using the iron-coated biochar, which ensured the stable operation of the initial stage of AD [66].

In contrast to previous studies, Lü et al. found that biochar mitigated

ammonia inhibition through biochemical rather than physical effects, using biochar of different particle sizes, to alleviate the inhibition of glucose digestion by ammonia nitrogen [67]. Here, biochemical effects promote microbial growth either by facilitating DIET, due to abundant functional groups on the biochar surface, or through the porous structure of biochar. Kizito et al. found that within the concentration range of 250–1000 mg/L ammonia nitrogen in the AD liquid of pig manure, the adsorption rate of wood biochar and rice husk biochar to ammonia nitrogen can reach 80.0 %, and even under higher load (the concentration of ammonia nitrogen reaches 1400 mg/L), the ammonia nitrogen adsorption rate can also reach 50.0 % [68].

Zhang et al. added nZVI-BC to an anaerobic co-digestion of sludge and kitchen waste system [69]. Here, the ability of nZVI-BC to alleviate ammonia inhibition in AD is mainly attributed to the cation exchange properties of carbon materials, hydrogen bonding between organic functional groups and ammonium ions, and the fact that the nZVI improves DIET. Lu et al. found that the application of biochar alone in chicken manure AD did not significantly alleviate the inhibition of high ammonia (5 g/L) [70]. Yet the porous structure of the biochar increased the abundance of *Firmicutes*, an acetate bacterium that plays a major role in acidogenesis and methanogenesis by 28.0-54.0 %. Subsequently, after loading nFe₃O₄ on biochar, the methane production rate of the system was greatly improved. The presence of nFe₃O₄ increased the tolerance of microorganisms to high ammonia concentrations and alleviated the inhibitory effect of ammonia on AD performance. Usually, in the early stage of AD, with the hydrolysis of protein, the ammonia nitrogen concentration will go through a stage of rapid increase. But Ning et al. found no significant increase in the ammonia nitrogen concentration after adding phosphoric acid-modified biochar (PBC) and PBC loaded with nZVI to the AD treatment of corn stover [71]. On the one hand, these two modified biochars enrich microorganisms, increase microbial activity and abundance, and convert part of ammonia nitrogen into biological available nitrogen. On the other hand, phosphoric acid modification increases the acidic functional groups on the surface of biochar, which is beneficial to adsorption of ammonia. Su et al. used four different modified biochars (iron, chitosan, iron-chitosan, iron-magnesium-chitosan) to reduce the initial ammonia nitrogen concentration of the kitchen digestive juice from 1600 mg/L to 1000 mg/L [72]. The amino group and hydroxyl group on the surface of chitosan form a stable complex with the added metal ions, which can improve its adsorption performance. In addition, it can also adsorb ammonia nitrogen cations through electrostatic interaction [73].

In general, the removal mechanism of ammonia nitrogen by ironbased and carbon-based nanomaterials in AD mainly covers key processes such as adsorption, chemical reaction, biological reduction, and ion exchange. However, it can be seen from Table 3 that the dosage of iron-based and carbon-based nanomaterials in AD is not clear. This stems largely from the relatively recent nature of the research field and the complexity of nanomaterials. The application of nanomaterials involves many variables, including the type of nanomaterial, particle size, surface properties, water quality conditions, treatment systems, etc. Under different experimental conditions, the optimal dosage of nanomaterials may be different, and future research needs to deeply explore the long-term impact and possible environmental risks of nanomaterials. Despite the uncertainty of dosage, looking forward to the future, ironbased and carbon-based nanomaterials, as a potential environmental treatment technology, still have great application prospects. With the continuous development and in-depth research of science and technology, we are expected to better understand the mechanism of action of nanomaterials and determine more precise dosage, to achieve a more efficient and sustainable AD process and make positive contributions to the protection of water bodies and the environment.

The level of VFAs is a major indicator of the stability of the digestive system during AD. VFAs are key intermediates in the production of methane, and a certain concentration of VFAs are required for methanogenesis during AD treatment. When the concentration of ammonia nitrogen in wastewater is too high, the growth of acid-producing bacteria will be significantly inhibited, and the production rate of VFAs will decrease, thereby affecting methane production. Therefore, by controlling the rate of VFAs production, the effects of ammonia inhibition can be mitigated. For example, R., Wang et al. added activated carbon and nZVI to an anaerobic reactor, and found that activated carbon enriched the abundance of two acid-producing bacteria, Trichococcus and norank_f_Bacteroidetes_vadinHA17 [44]. This is explained by the porous structure of activated carbon, which enhances enzyme activity during lactate and propionate production. The addition of nZVI increased the activity of pyruvate formate lyase during formic acid production and promoted the conversion of formic acid into acetic acid. Ajayi-Banji found that the addition of nFe₃O₄ reduced the acetic acid concentration of the system by at least 28 % and promoted the conversion of VFAs [52]. This also inhibited the adverse effects of acidification and free ammonia on the system. As a consequence, the system redox potential and the reproducibility of methanogens increased significantly. Johnravindar et al. added different types of biochar to the kitchen-sludge co-digestion system and found that miscanthus straw biochar had the best performance, which could reduce the accumulated VFAs from the highest 28.6 g/L to 2.9 g/L, which was 2.6 times of the control group [15]. The degradation tendency of rice husk biochar and sewage sludge biochar was also better than that of the control. In addition to the physical properties of biochar itself, the aromatic C-C and C-O bonds on the surface of biochar also matter, because the presence of these functional groups accelerates the electron transfer between bacteria and methanogens, thus promoting VFAs degradation [77].

Ragasri et al. added granular iron hydroxide nanomaterials (GNOF) to an activated sludge AD treatment experiment and found that the mean level of VFAs was higher than that of the control group for all six cycles and that iron promoted sludge hydrolysis [78]. Mostafa and Seongwon obtained more methane production from the AD of oleic acid by adding nFe_3O_4 and carbon nanotubes, which were 1.5 times more efficient in converting butyric acid to methane [79].

Mostafa and Tolba added nFe_3O_4 , multi-walled carbon nanotubes, and a composite of these to an activated sludge AD experiment and found an increase of the substrate degradation efficiency by 21.1 %, 18.3 % and 24.4 % respectively [79]. This is explained by the high specific surface area of carbon nanotubes and by providing a source of metal ions. Li et al. also found that the addition of 200 mg/L of magnetic carbon catalyzed the hydrolysis of refractory organic matter, and significantly reduced the accumulation of short-chain fatty acids during AD by increasing DIET, thus avoiding system acidification [80]. Therefore, the addition of these nanomaterials increases the conversion rate of VFAs while increasing the generation of VFAs. On the one hand,

Table 3

The role of iron-based and carbon-based nanomaterials in alleviating ammonia-
nitrogen inhibition.

Type of Nanomaterials	Substrate	Dosage	Effect	References
nZVI	Excess sludge	1.0 g/L	Maintain ammonia nitrogen concentration at	[42]
nZVI	Activated sludge	1.0 g/L	600–800 mg/L Total ammonia concentrations were reduced by 18.64 %. Maintain ammonia nitrogen	[61]
nZVI	Food waste*	2.0 g/L	concentration at 545 mg/L Total ammonia concentrations were reduced by 29.7 %	[63]
S-nZVI			Total ammonia concentrations were reduced by 38.8 %	
nZVI	Food waste	4–40 mg/ g TS _{added}	The addition of nZVI could regulate the concentration of ammonia nitrogen.	[74]
nZVI nFe ₃ O ₄	Thermal hydrolysis pretreatment activated sludge	10mmol	Effectively promoting the anti toxic activity of microorganisms during the ammonia inhibition stage	[75]
Pinewood biochar White oak biochar	Activated sludge	4.97 g/g dry matter of sludge 4.40 g/g dry matter	Significantly reduce fluctuations in ammonia nitrogen concentration during high- temperature AD	[76]
Carbon	Anaerobic	of sludge 1.0 g/L	and decreases the free ammonia by 10.5 % Accelerate the	[65]
nanotube	sludge		recovery of methane production performance	
Iron-coated biochar	Swine manure*	20 g/L	Maintain 94 % of the methanogenesis efficiency under high ammonia nitrogen stress	[66]
Fruitwoods biochar	Glucose	10 g/L	Biochar promotes methanogenesis under high ammonia nitrogen stress	[67]
Wood biochar Rice husk	Piggery manure	1.0 g/L	The maximum adsorption capacity for ammonia nitrogen is 44.64 mg/g (60 % adsorption rate) The maximum	[68]
biochar			adsorption capacity for ammonia nitrogen is 39.8 mg/g (53 % adsorption rate)	
nZVI- biochar (corn straw)	Food waste	3.1 g/ gTS	Total ammonia concentrations	[57]

(continued on next page)

Table 3 (continued)

Type of Nanomaterials	Substrate	Dosage	Effect	References
nFe ₃ O ₄ biochar (corn straw)	Chicken manure	0.15 g/g dry weight	were reduced by 41.65 % Relieve ammonia inhibition	[70]

* Ammonia chloride amended.

the increased VFAs can alleviate ammonia inhibition; and on the other hand, the addition of nanomaterials improves the conversion of VFAs so that no acidification of the system occurs.

Nanomaterials can remove free ammonia through adsorption and oxidation on the one hand, reduce the inhibitory effect of ammonia on AD performance, and thus reduce the toxic effect of ammonia on microorganisms. On the other hand, it promotes the metabolic activity of microorganisms in AD, reduces the accumulation of VFAs, and thus alleviates the inhibitory effect of ammonia.

1.1.3. Inhibition by hydrogen sulfide in the nanomaterials enhanced AD process

H₂S is formed by sulfate reduction during the AD process and is a component of the produced biogas. The content of H₂S in biogas should be as low as possible because H₂S is toxic to the environment and impairs biogas applications [81]. The production of H₂S in anaerobic reactors causes problems such as odor in the anaerobic unit area, severe corrosion at the gas-water interface in anaerobic systems, and reduced biogas quality, hence it is necessary to inhibit H₂S production during the AD process. The basis that nanomaterials can control H₂S concentration in the AD process is that they can enhance DIET, thereby changing the direction of electron flow and allowing methanogens to obtain more electrons [82]. The special structure and surface properties of nanomaterials can enhance the reactivity of pollutants for rapid conversion, thereby accelerating the oxidative decomposition process of H₂S by converting it into milder oxides [83,84]. In addition, nanomaterials can also absorb H₂S in organic wastewater, thereby reducing its concentration and reducing its release to the environment.

Specifically, nanomaterials such as iron-based nanomaterials and iron oxide nanomaterials are widely used in the AD process. These nanomaterials have high activity and surface area in the environment, which can effectively control harmful gases such as H₂S. In addition, the choice of these nanomaterials is influenced by factors such as their price, stability, and ease of production and handling. Therefore, it is very important to select suitable nanomaterials to control the H₂S content in AD processes. For instance, the addition of 0.05–0.20 g/g TS of nZVI in the waste activated sludge anaerobic reactor induced a decrease of H₂S content from 300 mg N/m³ without nZVI dosage to 0.5–6.1 N/m³ with nZVI dosage in 20 days [84]. This is explained by the formation of FeS, \mbox{FeS}_2 and S^0 by reduction of \mbox{H}_2S on the shell surface of nZVI. In an aqueous environment, the surface of nZVI forms an oxide layer consisting of two phases. Among them, the phase near the metal core is Fe (II)/Fe(III) mixed phase, while the phase near the oxide/water interface is mainly composed of Fe(III). Hydroxide exposed to water always exists on the surface of the oxide layer, and these hydroxides can effectively remove H₂S in sludge. Ferric hydroxide can act as an oxidizing agent to oxidize H₂S to polysulphides and subsequently pyrite [85]. The research of Farghali et al. also came to a similar conclusion: Nano ferrous oxide removes dissolved sulfide from the system by forming ferrous sulfide precipitation [86]. They added three different concentrations of nano ferrous oxide into an AD reactor respectively, and found that all of them could significantly reduce the H₂S concentration in the reactor, and the cumulative reduction in the biogas tank was up to 53.52 %. However, compared with nanomaterials in the form of Fe(III), the control effect of nano ferrous oxide on hydrogen sulfide does not appear to be that good.

This is because nano ferrous oxide removes dissolved sulfide by precipitating to form FeS [87]. In contrast, nano-iron in the form of Fe (III) first oxidizes dissolved sulfide to S^0 , and then the reduced Fe(II) continues to react with the remaining dissolved sulfide to form FeS [88]. Therefore, nano-iron oxide is not as effective as nanomaterials in the form of Fe(III). Hassanein et al. applied Fe, Ni, and Co nanomaterials to treat poultry manure by an AD process, and found that the mixed nanomaterials with different concentrations can significantly reduce the generation of H₂S. While the maximum concentration of H₂S could be reduced by 100 % [48]. The reduction of H₂S was related to the increasing concentration of iron, nickel, and cobalt mixture composites, and H₂S was removed by the precipitation formed by FeS and/or NiS wit a strong linear relationship (R² was 0.997).

Shen et al. observed H₂S concentrations below 5 ppb in biogas from a reactor supplemented with biochar [89]. Similarly, the integration of straw biochar columns inside an anaerobic reactor resulted in the rapid removal of 89–98 % of H₂S, sulfides, and free sulfide [90]. This is likely due to adsorption on the biochar surface due to the presence of COOH, -OH, C=O, and minerals. This is related to the pyrolysis and carbonization process of biochar. As the pyrolysis temperature increases, biochar gradually loses surface functional groups such as OH-, C-bound oxygen and hydrogen atoms and has more COOH, -OH, C=O, and minerals, and these remaining functional groups cause higher H₂S adsorption. Tsui et al. observed an 80.0 % reduction in H₂S content after the application of biochar, with approximately 26.6 % of total electrons returning from H₂S production to methane production [91]. In the absence of sulfide, sulfate-reducing bacteria can use organic matter (such as acetic acid) as an electron acceptor for metabolism. They work by using some special enzymes to degrade organic matter into acetate, releasing electrons and protons at the same time. In the absence of sulfide, the final electron acceptors for sulfate-reducing bacteria are usually carbon dioxide or methyl compounds. In this process, methanogens can use these electrons to reduce carbon dioxide and methyl compounds to methane. Collectively, this syntrophic relationship between sulfate-reducing bacteria and methanogens enables the avoidance of H₂S formation while utilizing these electrons for methanogenesis.

Iron-modified biochar has also demonstrated good H₂S adsorption properties. Choudhury et al. found that biochar can effectively remove soluble sulfide in the matrix by adsorption [92]. Compared with no addition of biochar, maple biochar can adsorb 219 mg S^{2–}/g biochar of soluble sulfide, while maple biochar loaded with Fe(III) can adsorb soluble sulfide of 269 mg S^{2–}/g biochar. Iron and sulfur mainly exist in the form of FeSO₄·7H₂O, indicating that the adsorbed sulfide is mainly oxidized to sulfate.

As can be seen from Table 4, from the existing literature, iron-based and carbon-based nanomaterials can eliminate H_2S in AD. The use of iron-based or carbon-based nanomaterials to remove H_2S in AD is a research area that has attracted much attention. At present, the types and quantities of nanomaterials added to different treatment systems have not been determined. Future research should focus on different types of iron-based or carbon-based nanomaterials, considering the conditions and requirements of different waste treatment systems, finding the best dosage through experiments and simulations, and exploring the physicochemical properties and activities of different nanomaterials to ensure the efficient use of H_2S remove.

1.2. Applications and mechanisms of nanomaterials enhanced AD processes

Researchers have studied the potential mechanisms underlying the promotion of AD by biochar, and proposed various hypotheses [96]. For instance, the dissolution of nanomaterials provides microbial nutrients that enhance AD [97]. Here we present the main mechanisms that improve microbial community response, interspecies electron transfer, and extracellular polymer changes by nanomaterial addition.

Table 4

The potential of iron- and carbon-based nanomaterials for hydrogen sulfide removal during anaerobic digestion.

Type of Nanomaterials	Substrate	Dosage	Effect	References
nZVI	Waste activated sludge	0.20 g/ g TS	The removal efficiency of hydrogen sulfide is 99.8 %	[84]
nzvi	sulfate wastewater	5 g/L	Sulfate reducing bacteria utilize ferrous ions to reduce hydrogen sulfide concentration	[93]
Nano ferrous oxide	Cattle manure	1000 mg/L	The removal efficiency of hydrogen sulfide is 53.5 %	[86]
nFe ₃ O ₄	Poultry litter	1000 mg/L	The removal efficiency of hydrogen sulfide is 100 %	[48]
nFe ₃ O ₄	Swine manure	75 mmol	Reduce approximately 70 % sulfate concentration in the system	[94]
Wood-derived biochar	Chicken manure	5 % of TS	The hydrogen sulfide content has decreased by over 95 %	[95]
Corn stover biochar	Anaerobic sludge	3.64 g/ g TS	Hydrogen sulfide removal rate greater than 94.4 %	[89]
Wood-derived biochar	Anaerobic sludge	/	The removal efficiency of gaseous H ₂ S is greater than 98 %	[90]
Wood chips biochar	Sewage sludge and leachate	/	Reduced H ₂ S content by 80 %	[91]
Corn stover biochar	Dairy Manure	1.82 g/ g TS	91.2 % reduction compared to the control	[92]
Maple biochar		1.82 g/ g TS	90.0 % reduction compared to the control	
Iron- impregnated corn stover biochar		0.50 g/ g TS	100 % reduction compared to the control	
Iron- impregnated maple biochar			97.5 % reduction compared to the control	

1.2.1. Microbial community response

Anaerobic methanogenesis results from the synergistic interaction of several microorganisms. The degree of degradation of organic matter depends on the activity of microorganisms. The presence of nanomaterials can optimize the microbial community, in particular by enriching microorganisms possessing the DIET capability, thus promoting anaerobic methanogenesis. Xie et al. analyzed the microbial community changes when nFe₃O₄ was used in AD of sludge [98]. The results show that nFe₃O₄ can increase the abundance of Fibrobacter from 1.5 to 8.2 %. Fibrobacter hydrolyzes cellulose into small molecular carbohydrates. At the same time, the abundance of acetoclastic methanogens (such as Methanosaeta) increased 1.78 times. nFe₃O₄ facilitates AD by reshaping the microbial colony, i.e., enriching the relevant flora of the hydrolysis stage and acetoclastic methanogenesis [93]. Kaur et al. also found that nFe₃O₄ could enrich more genus Enterococcus, Methanosaeta and Methanosarcina during the AD of Azolla microphylla [99]. Enterococcus belongs to Phylum Firmicutes and can ferment cellobiose into lactic acid and then oxidized into acetate. Most of the genes in the reactor that determine the carbohydrate-active enzymes used by

microorganisms to decompose plant biomass come from *Firmicutes* [100]. The KEGG database also shows that the abundance of genes encoding *acetate kinase* and *phosphate acetyltransferase* used by *Methanosarcina* is much higher than that of the control [101]. Zhou et al. also found that nFe₃O₄ can promote the activities of key enzymes such as *hydrolase, dehydrogenase, acetate kinase*, and *coenzyme* F_{420} during AD [102]. This further proves the previous conclusion that nFe₃O₄ can enrich bacterial groups related to hydrolysis and acetoclastic methanogenesis.

Guang Yang et al. found that nZVI could significantly increase the abundance of Clostridium sensu stricto, Proteiniphilum, Fonticella and Pygmaiobacter in the AD system [103]. These bacteria are all related to the production of VFAs. From the gene analysis of substrate metabolism and VFAs formation in the KEGG database, nZVI promotes the abundance of genes related to hydrolysis, membrane transport and acidogenesis processes, fundamentally increasing the production rate of VFAs. Tao Wang et al. found that adding nZVI, nano-iron oxide (nFe₂O₃) could double the gene copy number of bacteria and archaea in the AD system, producing more α -Proteobacteria, β -Proteobacteria, Bacteroidetes and Methanosaeta [104]. Qiao Wang et al. also found that Pseudomonas veronii appeared in the sludge AD system with nano ferric oxide (nFeO) dosage of 200 mg/L [105]. It not only has strong hydrolysis ability, but also dominates the iron reduction process [106]. And whether it is nFeO, nZVI, or nFe₃O₄, it can increase the activity of key hydrolysis enzymes such as Alcohol dehydrogenase 4, D-lactate dehydrogenase, and Pyruvate dehydrogenase E1 component. P., Wang et al. studied the effect of nZVI, nFe₂O₃ and nFe₃O₄ on AD treating food waste [45]. In terms of microorganisms, Proteiniphilum and Fermentimonas associated with hydrolysis and acetogenesis processes were greatly increased compared with the control, indicating that these three nanomaterials promote the processes of hydrolysis and acetogenesis. In terms of archaea, Methanosaeta and Methanosarcina, the two kinds of methanogens related to acetoclastic methanogens, also increased significantly, with a total abundance of up to 94.1 %, which indicated that the above three materials were mainly enriched in acetoclastic methanogens rather than hydrogenotrophic methanogens. In addition, the three pilin-encoding genes *mshA*, *mshB*, and *mshC* were only detected in the reactor adding nZVI, nFe₂O₃ and nFe₃O₄, suggesting that these three materials effectively enhanced the DIET potential. Like nFe₃O₄, most other iron oxides such as nZVI promote AD by enriching bacteria or archaea in the hydrolysis stage and acetoclastic methanogenesis stage, thereby promoting the production of key enzymes.

Pytlak et al. showed that wood biochar can enrich Prevotella in Bacteroidales in the sugar beet waste AD system [107]. Prevotella can participate in hydrolysis [108] and acetogenesis [109], and the abundance of Prevotella was positively correlated with the gene responsible for the synthesis of carbon monoxide dehydrogenase related to the acetate-generating Wood-Ljungdahl pathway. Unlike iron-based nanomaterials enriched in acetoclastic methanogens, the substrate digestion fluid "directly stimulated" by biochar is enriched in hydrogenotrophic methanogens, and their methanogenic capacity is higher, which the authors speculate is related to biochar-mediated DIET [110]. During the AD of cow manure, Su Wang et al. also found that rice straw biochar greatly increased the abundance of Methanomassiliicocus and Methanoculleus (hydrogenotrophic methanogens) while reducing the abundance of Methanosaeta (acetoclastic methanogens) [111]. Although the system is dominated by acetoclastic methanogens, the KEGG database shows that the relative abundance of genes related to acetoclastic methanogenesis decreased by 67.9 %, while the relative abundance of genes related to hydrogenotrophic methanogenesis increased by 44.6 %, which further proves that biochar can enrich hydrogenotrophic methanogens. G., Wang et al. stated that under high ammonia nitrogen stress in swine manure, sawdust biochar can enrich Methanosarcina and Methanobacterium and relieve ammonia inhibition [112]. The methanogenesis pathway based on the KEGG database shows that hydrogenotrophic methanogenesis contributes the most to methane

production. *Geobacter* can participate in methanogenesis through the DIET pathway [113]. Cai et al. stated that during the AD of pig manure, high-throughput results and quantitative polymerase chain reaction results showed that biochar can significantly increase the absolute abundance of *Geobacter* [114]. In addition, under the ammonia stress of chicken manure, biochar can specifically enrich *Methanoculleus* and *Methanospirillum*, secreting enzymes related to some hydrogenotrophic methanogenesis, such as the Formylmethanofuran-tetrahydromethan opterin N-formyltransferase, methenyltetrahydromethanopterin cyclohydrolase, and formylmethanofuran dehydrogenase subunit A, thus adapting to the ammonia stress and takes a dominant position in the digestive system [115]. In general, in AD systems, biochar can enrich acetoclastic methanogens.

To this end, we summarized the effects of modified biochar based on iron materials on changes in AD microbial communities. Chen et al. found that magnetite-loaded biochar could enrich more Ruminococcaceae and a small amount of Pseudomonas and Geobacter, which are all electroactive bacteria [116]. In addition, the abundance of Methano*thrix*, which is an acetoclastic methanogen but can utilize H^+ and $e^$ produced by DIET for methane production, was higher in the reactor with magnetite-loaded biochar dosed [117]. Methanosarcina was also enriched, with the highest abundance. As mentioned earlier, Methanosarcina is capable of acetoclastic methanogenesis and hydrogenotrophic methanogenesis, and can directly accept electrons to produce methane through DIET [62]. The KEGG database results showed that acetoclastic methanogenic and hydrogenotrophic methanogenic genes increased by 49.9 % and 35.1 % respectively. This illustrates the dual effect of magnetite-loaded biochar on AD. Lim et al. studied the effect of iron-modified biochar (nZVI-BC) on the AD of food waste [118]. Compared with the control group, in the reactors dosed with nZVI, BC and nZVI-BC, the bacteria of Firmicutes related to hydrolysis increased. But in terms of archaea, pure biochar enriched more Methanoculleus, nZVI enriched more Methanosaeta, while nZVI-BC enriched more Methanosarcina.

X., Wang et al. used KEGG database to identify genes for key enzymes associated with different methanogenesis pathways [119]. In nZVI-BC-mediated high-temperature (55 \pm 1 °C) AD of food waste, the absolute abundance of genes related to acetoclastic methanogenesis increased by up to 28.56 %., and the absolute abundance of genes related to hydrogenotrophic methanogenesis increased by up to 75.29 %. Similarly, the abundance of enzymes related to methane metabolism such as formylmethanofuran dehydrogenase, formylmethanofurantetrahydromethanopterin Nformyltransferase, and methenyltetrahydromethanopterin cyclohydrolase also increased by 47.25 % compared with the control. In addition, the reactor added with nZVI-BC had higher Thermotogae [120] and Methanothrix [121], which are related to carbohydrate degradation and methanogenesis respectively. Overall, nZVI-BC can increase the abundance of functional genes and enzymes in hydrolysis and methanogenesis stages. Wang and Yu also found that after adding nZVI-BC to the AD of food waste, the abundance of Methanothrix increased by 23.09 %, while the proportion of Methanobacterium decreased by 21.13 % [122]. The KEGG database results found that the relative abundance of hydrogenotrophic methanogenic pathway decreased by 4.9 %, while the relative abundance of acetoclastic methanogenic pathway increased by 2.8 %. Various evidences show that the addition of nZVI-BC seems to contribute more to the acetoclastic methanogenic pathway, followed by the hydrogenotrophic methanogenic pathway.

Overall, the addition of nanomaterials enriched acetoclastic methanogens in the system and promoted performances of the AD process, but nanomaterial-mediated DIET methanogenesis also made a partial contribution. It provides a large surface area and specific chemical properties to facilitate the attachment and growth of microorganisms. At the same time, it can be used as an electron transfer medium in the microbial community to help the electron transfer between microorganisms. In addition, the combined effects of adjusting the pH value and microenvironment, and serving as a transport medium for nutrients can optimize the structure and function of the microbial community and improve the efficiency and stability of the AD process.

1.2.2. Direct interspecies electron transfer

During the AD process, efficient electron transfer is crucial for the interaction of different microorganisms and directly affects substrate digestion [123]. DIET could be facilitated by conductive nanomaterials, thus increasing the rate of methane production [124]. In the absence of nanomaterials, DIET is done by conductive pili and cytochromes, and is thus limited by the size and abundance of pili and cytochromes (Fig. 3A). Addition of conductive nanomaterials such as carbon and iron nanomaterials accelerates electron transfer because nanomaterials are highly conductive and have a large specific surface area. As shown in Fig. 3B, C, iron-based and carbon-based nanomaterials can form electron channels between microorganisms, forming a similar effect to conductive pili and cytochromes. This results in a faster DIET rate and higher efficiency of anaerobic methanogenesis [125]. F., Liu et al. found that in the presence of granular activated carbon, G. metallireducens and G. sulfurreducens *bacilli* formed a direct electrical connection (Fig. 3B) [126]. Kato et al. found that nFe₃O₄ can extend the conductive pili of microorganisms and make the microbial population conductive [21]. Rotaru et al. found that the co-culture of Geobacter metallireducens and Methanosarcina barkeri in granular activated carbon even replaced pili for electron transfer [127].

Nanomaterials also reduce the energy consumption of electrogenic species involved in DIET, while extracellular electron transfer is enhanced in methanogens. Zhu et al. found that microorganisms that have extracellular electron transfer capabilities are enriched in the presence of conductive iron materials [128]. The extracellular proteins of their cells contain amide groups and hydrogen bonds that can transfer electrons to participate in long-range electron transfer (Fig. 3C). Xie et al. demonstrated that magnetite nanomaterials and graphite powder additives enhanced DIET by increasing the abundance of methane-oxidizing bacteria and methanolic bacteria [98]. Li et al. focused on the enhancement of AD performances with nZVI/activated carbon dosage, in terms of enhanced phenol removal, organic matter degradation, and methane production [129]. In the presence of nZVI/activated carbon, CO2 is not reduced by H2 but receives electrons directly and is reduced to methane in the presence of methanogens [130, 131]. In summary, nanomaterials with good electrical conductivity can improve the DIET efficiency of hydrogen-producing and methanogenesis, while organic matter conversion and methane production can also be improved.

Microbial quorum sensing is an information exchange mechanism between species other than DIET, which achieves information transmission by producing signaling molecules to stimulate the expression of specific genes [132]. Quorum sensing of methanogens is similar to secretion of Gram-negative bacteria, affecting the cell assembly and carbon metabolism flux of methanogens by regulating secreted N-acyl-homoserine lactones (AHLs) [133]. There is evidence that exogenous AHLs promote the production of coenzyme $\mathrm{F}_{420},$ enhance the methanogenic capacity of anaerobic granular sludge, and regulate the community structure of bacteria and methanogens by adjusting extracellular polymers [134]. Moreover, Pearson correlation shows that functional bacterial flora at each stage of AD are significantly related to certain AHLs signals, such as hydrolytic-fermentative bacteria and C4-HSL and OXOC6-HSL, C14-HSL and aceticlastic methanogenesis and hydrogenotrophic Methanogenesis is significantly related [135]. In addition, H., Dang et al. also found that more AHLs were detected in the blackwater AD reactor supplemented with granular activated carbon compared with the control [136]. This is consistent with the methanogenic performance, probably because the abundance of Methanosaeta on suspended sludge and granular activated carbon biofilms is much higher than the control. Granular activated carbon may modulate the abundance of Methanosaeta through quorum sensing, since microorganisms

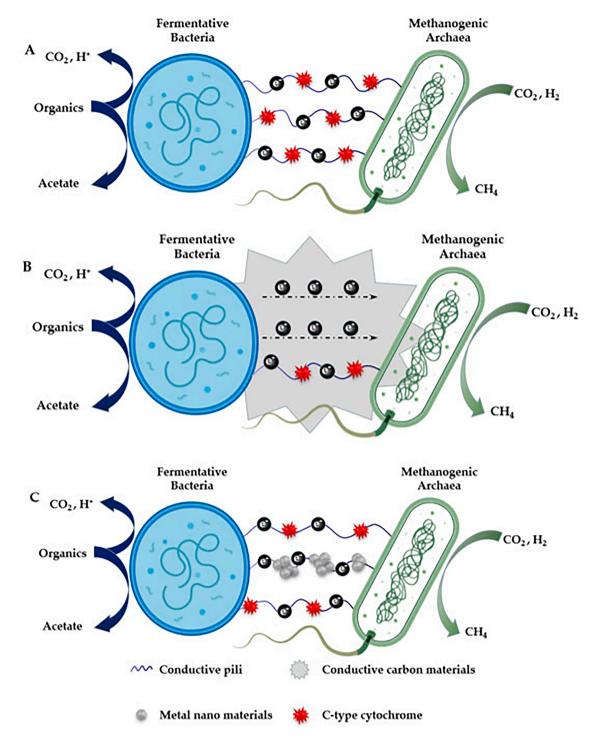


Fig. 3. Mechanisms by which (A) conductive pili and C-type cytochromes promote direct interspecies electron transfer (DIET), (B) conductive carbon materials promote DIET, and (C) conductive iron materials promote DIET.

such as *Pseudomonas, Geobacter*, and *Methanosaeta* have been shown to efficiently produce AHLs [133,135,137]. *Pseudomonas, Geobacter* was shown to be an electroactive bacterium that promotes DIET of *Methanoshrix* (family *Methanosaeta*) through e-pili or c-type cytochromes omcS [138]. The *Pseudomonas, Geobacter* and *Methanosaeta* mentioned here have been shown to be effectively enriched by iron-based or carbon-based nanomaterials in the previous section. Therefore, as typical conductive materials, DIET mediated by iron-based and carbon-based nanomaterials can affect the release of signaling molecules in AD systems [139]. In addition to AHLs directly related to methanogens, other signaling substance genes such as autoinducer-2 (AI-2),

diffusible signal factor (DSF), and 3'-5'cyclic diguanosine monophosphate (c-di-GMP) also play an important role in AD of syntrophic microorganisms [140]. For example, the secretion of c-di-GMP can promote the production of type IV pili and promote the formation of biofilms [141]. Fig. 4 introduces the potential role of quorum sensing in syntrophic methane production, which also shows that conductive materials can promote the syntrophic methane production process. Conductive nanomaterials have been proven to replace c-Cyts and conductive pili as electronic connection devices, achieving long-distance electron transmission and accelerating the DIET phenomenon [142]. Therefore, the addition of conductive nanomaterials can have a certain

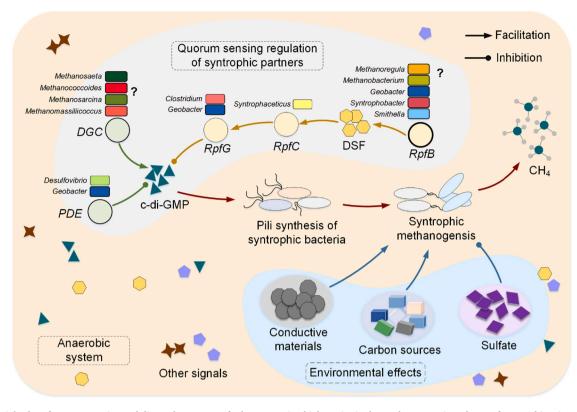


Fig. 4. Potential roles of quorum sensing and direct electron transfer between microbial species in the methanogenesis pathway of syntrophic microorganisms. The entire yellow area represents the AD process. The gray area represents the quorum sensing effect of syntrophic microorganisms, the circles represent different quorum sensing signal molecules, and the rectangles represent different microorganisms related to the methanogenesis process. The blue area represents the influence of other factors such as conductive materials on the methanogenesis process. The two different arrows represent facilitation and inhibition respectively. The figure has been authorized for publication.

impact on the secretion of quorum sensing signal molecules, thereby improving AD, but the specific mechanism requires further research.

Extracellular polymers (EPS) are polymers excreted by microorganisms, accounting for 80 % of the mass of activated sludge, and represent a crucial medium for the exchange of electrons between the inner and outer cell lavers [143]. He et al. found a 30 % increase in methane production when exposed to 30 mmoL/L nZVI [139]. This suggested that the additional dihydrogen released by nZVI oxidation could stimulate the hydrogenotrophic methanogens. The nZVI particles did not enter the interior of the sludge particles but were adsorbed on the surface of the anaerobic granular sludge in the form of iron oxide aggregates [43]. This protected most microbial cells from contact damage. In addition, the extracellular polymers located on the outer surface of the anaerobic sludge particles can react with nZVI. This accelerates the corrosion of nZVI and reduces the release of dihydrogen during nZVI dissolution. Thus, the toxicity of nZVI to anaerobic microorganisms is further attenuated. Rapid hydrogen production and accumulation following nZVI dissolution can inhibit methanogenesis, while slow dihydrogen release can increase methanogenesis [144,145].

Ye et al. found that the addition of Fe_2O_3 significantly promoted extracellular polymer production and increased cytochrome concentration, resulting in a 35.52 % increase in methane production [146]. The formation of large and dense bioaggregates and the increase of cytochromes accelerated the direct electron exchange between coprophilous and methanogens [147]. The concentration of humic substances increased significantly after nanomaterials dosage in the study, which reduced the amount of total VFAs, and produced more redox-active mediators that participated in the interspecies electron transfer process through intermediary pathways, thus promoting anaerobic methanogenesis [148]. Therefore, extracellular polymers can store electrochemical energy in sludge and can effectively improve the DIET process, which ultimately enhances anaerobic methanogenesis.

2. Inactivation of antibiotic resistance genes by nanomaterials

The overuse of antibiotics and various antimicrobial drugs in human health and livestock farming etc. is a major health issue since it could accelerate the proliferation of antibiotic-resistant bacteria that diffuse antibiotic-resistance genes in environmental media [149]. The spread of antibiotic resistance genes in environmental media may represent a higher environmental hazard than antibiotics themselves [150,151]. Pathogenic microorganisms can acquire antibiotic resistance genes by vertical or horizontal gene transfer [152,153]. Vertical gene transfer is essentially a self-replication process of resistant microorganisms carrying antibiotic resistance genes. Horizontal gene transfer is mainly driven by mobile genetic elements such as plasmids, transposons, or phages, which are capable of spreading between conspecifics and heterospecifics, and even between resistant and non-resistant microorganisms [154]. Antibiotic resistance genes can remain in various organic wastes such as sewage sludge [155], livestock and poultry manure [156], and kitchen waste [157]. If not disposed of properly, antibiotic resistance genes can quickly spread in large numbers in the human environment and pose a serious risk to human health.

Nanomaterials can reduce gene transfer by immobilizing organisms or inhibiting the growth of drug-resistant microorganisms [158]. For instance, the addition of 160 mg/L nZVI reduced the absolute and relative abundance of antibiotic resistance genes by 5.5–9.4 and 2.0–6.3 logs, respectively, during the AD of cattle manure [159]. Results of redundancy analysis showed that the content of antibiotic resistance genes was directly correlated with the changes in mobile genetic elements. 160 mg/L nZVI reduced the content of four mobile genetic elements, *IntI1, InTI2, Tn916/ 1545* and *ISCR1* by 15.1 %. The gene copy

number of Tn916/1545 (the highest content) was 8.95 logs lower than that of the control.

P., Wang et al. obtained antibiotic resistance genes removal rates of up to 86.64 % and 31.08 % in high and low-temperature AD reactors for kitchen waste disposal respectively [46]. Results showed that the reduction in the content of antibiotic resistance genes after the addition of nZVI was significantly correlated with the abundance of Firmicutes, which dominated the process. The antibiotic resistance gene content decreased as Firmicutes abundance decreased from 35.47 to 25.35 % at high temperatures, and from 25.62 to 21.47 % at medium temperatures. Streptococcus is the host of a macrolide resistance gene that positively correlates with intI1 [160]. The relative abundance of Streptococcus, the dominant microorganism belonging to phylum Firmicutes genus in the anaerobic digestive system, decreased from 9.74 to 0.56 % at medium temperature (35 °C), and from 0.19 to 0.17 % at high temperature (55°C) after the addition of nZVI. Lu et al. used Procrustes analysis to find that microbial communities and mobile genetic elements contributed 37.0 % and 58.9 % to the variation of antibiotic resistance genes respectively [161]. Therefore, the addition of nZVI influences the changes in antibiotic resistance genes by inducing changes in microbial communities and mobile genetic elements [141].

Yang et al. found that the relative abundance of most antibiotic resistance genes detected in pig manure AD systems could be reduced by more than 85 % at 5-10 % biochar dosage treatment, and that the removal of IntI1 could be increased by 15 % at 5 % biochar dosage treatment [162]. The addition of biochar had a significant impact on the bacterial community by reducing the relative abundance of antibiotic resistance genes of bacteria. This was related to the porous structure of the biochar, which was able to immobilize microorganisms by adsorption and reduce microbial exchange, thus reducing horizontal gene transfer. In contrast to previous studies, Li et al. applied biochar and nZVI-BC to the AD of sludge and found that both could reduce sludge antibiotic resistance genes, with nZVI-BC addition producing a better effect than biochar dosage alone [163]. Because compared with ordinary biochar, the specific surface area of nZVI-BC is greatly increased, which is beneficial to inducing the oxidative stress response of microorganisms, increasing the antioxidant capacity of microorganisms, and reducing the inheritance of ARGs. At the same time, the higher the antioxidant capacity, the less favorable it is for the occurrence of DNA damage-induced responses, leading to severe damage to the cell membrane and inhibiting the horizontal transfer of ARGs. In addition, NH₄⁺-N promoted horizontal gene transfer of antibiotic resistance genes, while biochar and nZVI-BC reduced NH₄⁺-N content in the system, alleviating the phenomenon of ammonia stress [164] and effectively removing Sul1 with antibiotic target replacement as the resistance mechanism.

The study by Yue Lu et al. and Shuo Yang et al. also showed that the removal rate of antibiotic resistance genes was significantly correlated with the methane production of AD, and a higher removal rate of antibiotic resistance genes brought about more methane production [161, 162]. Given the excellent synergistic performance of the composite material with nano-iron and biochar, composite nanomaterials can effectively remove antibiotic resistance genes from the digestive system while enhancing AD performance, which should be a promising development direction for the future.

3. Conclusion

This review paper comprehensively summarizes the diverse roles of nanomaterials in the AD process. The findings endorse that nanomaterials enhance AD either by promoting acetoclastic methanogenesis or hydrogenotrophic methanogenesis. From the perspective of various dosages of nanomaterials that promote biogas production or methane content, nFe_3O_4 seems to be the best choice. The latter, which utilizes H_2 and CO_2 in biogas, has the potential to increase methane yield and presents a promising direction for future development due to its ability to purify biogas in situ. The mechanistic analysis uncovers the

transformative impact of nanomaterials on microbial community structure, modification of extracellular polymeric properties, and reinforcement of interspecies electron transport. Furthermore, the investigation delves into the risk-controlling role of nanomaterials in curtailing the dissemination of antibiotic resistance genes. These discoveries underscore the potential of nanomaterials in optimizing and augmenting the efficiency of AD. Nevertheless, further exploration of the long-term implications of nanomaterials on the environment and ecosystems is imperative to ensure their sustainable application and safety. Studies on the synergistic relationship between composite nanomaterials, such as magnetic iron-carbon composites, and their interaction with microorganisms in the AD system, are necessary to avoid possible hazards in the application of composite nanomaterials. Overall, this study offers valuable insights to advance the application of nanomaterials in the realm of AD.

Currently, iron-based and carbon-based nanomaterials are mainly used in AD. In the future, more types of nanomaterials, such as metal sulfides and metal organic frameworks (MOFs), can be explored and developed to improve catalytic efficiency and adsorption performance. Meanwhile, one can focus on designing nanomaterials with multifunctional properties to meet the needs of different AD. These multifunctional nanomaterials can not only promote biogas production and methane content, but also resist risks posed by various novel pollutants such as antibiotic resistance genes, thereby improving waste treatment efficiency. On the other hand, in future researches, attention should also be paid to the sustainability and environmental friendliness of nanomaterials. This includes research on green synthesis methods, utilization of renewable resources, recycling of waste to reduce adverse impacts on the environment.

Declaration of Competing Interest

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

Data availability

Data will be made available on request.

Acknowledgments

The authors would like to acknowledge the co-funding of this work by Projects of International Cooperation Shanghai (STCSM, 23230711300) and the Natural Science Foundation of Shanghai (No.22ZR1443200).

References

- Y. Jian, W.B. Liu, Research on China's renewable energy strategic development strategy from the perspective of sustainable development, IOP Conf. Ser.: Earth Environ. Sci. 510 (2020), https://doi.org/10.1088/1755-1315/510/3/032026.
- [2] S. Kaza, L.C. Yao, P. Bhada-Tata, F.V. Woerden. What a waste 2.0: a global snapshot of solid waste management to 2050[C]. 2018.
- [3] B. Sharma, B. Vaish, U.K.S. Monika, P. Singh, R.P. Singh, recycling of organic wastes in agriculture: an environmental perspective, Int. J. Environ. Res. 13 (2019) 409–429, https://doi.org/10.1007/s41742-019-00175-y.
- [4] F. Deganello, A.C. Tavares, E. Traversa, Editorial: chemistry, a sustainable bridge from waste to materials for energy and environment, Front Chem. 8 (2020), 641129, https://doi.org/10.3389/fchem.2020.641129.
- [5] G. Náthia-Neves, M. Berni, G. Dragone, S.I. Mussatto, T. Forster-Carneiro, Anaerobic digestion process: technological aspects and recent developments, Int. J. Environ. Sci. Technol. 15 (2018) 2033–2046, https://doi.org/10.1007/s13762-018-1682-2.
- [6] R.M. Jingura, R. Matengaifa, Optimization of biogas production by anaerobic digestion for sustainable energy development in Zimbabwe, Renew. Sustain. Energy Rev. 13 (2009) 1116–1120, https://doi.org/10.1016/j.rser.2007.06.015.
- [7] Z. Ferdous, H. Ullah, A. Datta, A. Attia, A. Rakshit, S.H. Molla, Application of Biogas slurry in combination with chemical fertilizer enhances grain yield and

profitability of maize (Zea Mays L.), Commun. Soil Sci. Plant Anal. 51 (2020) 2501–2510, https://doi.org/10.1080/00103624.2020.1844728.

- [8] R. Nkoa, Agricultural benefits and environmental risks of soil fertilization with anaerobic digestates: a review, Agron. .Sustain. Dev. 34 (2013) 473–492, https:// doi.org/10.1007/s13593-013-0196-z.
- M.A. Ganzoury, N.K. Allam, Impact of nanotechnology on biogas production: a mini-review, Renew. Sustain. Energy Rev. 50 (2015) 1392–1404, https://doi.org/ 10.1016/j.rser.2015.05.073.
- [10] X.H. Qu, H.X. Zeng, Y.S. Gao, T.D. Mo, Y. Li, Bio-hydrogen production by dark anaerobic fermentation of organic wastewater, Front. Chem. 10 (2022), 978907, https://doi.org/10.3389/fchem.2022.978907.
- [11] Y. Chen, J.J. Cheng, K.S. Creamer, Inhibition of anaerobic digestion process: a review, Bioresour. Technol. 99 (2008) 4044–4064, https://doi.org/10.1016/j. biortech.2007.01.057.
- [12] K. Paritosh, M. Yadav, A. Chawade, D. Sahoo, N. Kesharwani, N. Pareek, V. Vivekanand, Additives as a support structure for specific biochemical activity boosts in anaerobic digestion: a review, Front. Energy Res. 8 (2020), https://doi. org/10.3389/fenrg.2020.00088.
- [13] H. Baniamerian, P.G. Isfahani, P. Tsapekos, M. Alvarado-Morales, M. Shahrokhi, M. Vossoughi, I. Angelidaki, Application of nano-structured materials in anaerobic digestion: current status and perspectives, Chemosphere 229 (2019) 188–199, https://doi.org/10.1016/j.chemosphere.2019.04.193.
- [14] F. Suanon, Q. Sun, M.Y. Li, X. Cai, Y.C. Zhang, Y.J. Yan, C.P. Yu, Application of nanoscale zero valent iron and iron powder during sludge anaerobic digestion: impact on methane yield and pharmaceutical and personal care products degradation, J. Hazard. Mater. 321 (2017) 47–53, https://doi.org/10.1016/j. jhazmat.2016.08.076.
- [15] D. Johnravindar, J.W.C. Wong, D. Chakraborty, G. Bodedla, G. Kaur, Food waste and sewage sludge co-digestion amended with different biochars: VFA kinetics, methane yield and digestate quality assessment, J. Environ. Manage. 290 (2021), 112457, https://doi.org/10.1016/j.jenvman.2021.112457.
- [16] M. Dehhaghi, M. Tabatabaei, M. Aghbashlo, H. Kazemi Shariat Panahi, A. S. Nizami, A state-of-the-art review on the application of nanomaterials for enhancing biogas production, J. Environ. Manage. 251 (2019), 109597, https://doi.org/10.1016/j.jenvman.2019.109597.
- [17] E.M. Abdelsalam, M. Samer, Biostimulation of anaerobic digestion using nanomaterials for increasing biogas production, Rev. Environ. Sci. Bio/Technol. 18 (2019) 525–541, https://doi.org/10.1007/s11157-019-09505-0.
- [18] S.Z. Khan, A.A. Zaidi, M.N. Naseer, H. Almohamadi, Nanomaterials for biogas augmentation towards renewable and sustainable energy production: a critical review, Front Bioeng. Biotechnol. 10 (2022), 868454, https://doi.org/10.3389/ fbioe.2022.868454.
- [19] Y.R. Zhang, Z.H. Yang, R. Xu, Y.P. Xiang, M.Y. Jia, J.H. Hu, Y. Zheng, W.P. Xiong, J. Cao, Enhanced mesophilic anaerobic digestion of waste sludge with the iron nanoparticles addition and kinetic analysis, Sci. Total Environ. 683 (2019) 124–133, https://doi.org/10.1016/j.scitotenv.2019.05.214.
- [20] G. Kassab, D. Khater, F. Odeh, K. Shatanawi, M. Halalsheh, M. Arafah, J.B. Van Lier, Impact of nanoscale magnetite and zero valent iron on the batch-wise anaerobic co-digestion of food waste and waste-activated sludge, Water (Basel) 12 (2020), https://doi.org/10.3390/w12051283.
- [21] S. Kato, R. Nakamura, F. Kai, K. Watanabe, K. Hashimoto, Respiratory interactions of soil bacteria with (semi)conductive iron-oxide minerals, Environ. Microbiol. 12 (2010) 3114–3123, https://doi.org/10.1111/j.1462-2920.2010.02284 x.
- [22] G.S. Aguilar-Moreno, E. Navarro-Cerón, A. Velázquez-Hernández, G. Hernández-Eugenio, M.Á. Aguilar-Méndez, T. Espinosa-Solares, Enhancing methane yield of chicken litter in anaerobic digestion using magnetite nanoparticles, Renew. Energy 147 (2020) 204–213, https://doi.org/10.1016/j.renene.2019.08.111.
- [23] Y.Y. Wang, D.L. Wang, H.Y. Fang, Comparison of enhancement of anaerobic digestion of waste activated sludge through adding nano-zero valent iron and zero valent iron, RSC Adv. 8 (2018) 27181–27190, https://doi.org/10.1039/ c8ra05369c.
- [24] Y. Hu, X. Hao, D. Zhao, K. Fu, Enhancing the CH4 yield of anaerobic digestion via endogenous CO₂ fixation by exogenous H₂, Chemosphere 140 (2015) 34–39, https://doi.org/10.1016/j.chemosphere.2014.10.022.
- [25] M. Zhang, J. Li, Y. Wang, Impact of biochar-supported zerovalent iron nanocomposite on the anaerobic digestion of sewage sludge, Environ. Sci. Pollut. Res. Int. 26 (2019) 10292–10305, https://doi.org/10.1007/s11356-019-04479-6.
- [26] M.R. Patel, N. Rathore, N.L. Panwar, Influences of biochar in biomethanation and CO₂ mitigation potential, Biomass Convers. Biorefinery (2021), https://doi.org/ 10.1007/s13399-021-01855-6.
- [27] H.B. Liu, X.K. Wang, Y.Y. Fang, W.J. Lai, S.Y. Xu, E. Lichtfouse, Enhancing thermophilic anaerobic co-digestion of sewage sludge and food waste with biogas residue biochar, Renew. Energy 188 (2022) 465–475, https://doi.org/10.1016/j. renene.2022.02.044.
- [28] R.C. Lin, J. Cheng, L.K. Ding, J.D. Murphy, Improved efficiency of anaerobic digestion through direct interspecies electron transfer at mesophilic and thermophilic temperature ranges, Chem. Eng. J. 350 (2018) 681–691, https:// doi.org/10.1016/j.cej.2018.05.173.
- [29] G.J. Wang, Q. Li, X. Gao, X.C. Wang, Synergetic promotion of syntrophic methane production from anaerobic digestion of complex organic wastes by biochar: performance and associated mechanisms, Bioresour. Technol. 250 (2018) 812–820, https://doi.org/10.1016/j.biortech.2017.12.004.
- [30] H.Y. Ma, Y. Hu, T. Kobayashi, K.Q. Xu, The role of rice husk biochar addition in anaerobic digestion for sweet sorghum under high loading condition, Biotechnol. Rep. (Amst) 27 (2020) e00515, https://doi.org/10.1016/j.btre.2020.e00515.

- [31] Q. Jiang, C. Zhang, P. Wu, P. Ding, Y. Zhang, M.H. Cui, H. Liu, Algae biochar enhanced methanogenesis by enriching specific methanogens at low inoculation ratio during sludge anaerobic digestion, Bioresour. Technol. 338 (2021), 125493, https://doi.org/10.1016/j.biortech.2021.125493.
- [32] J.T. Pan, J.Y. Ma, X.X. Liu, L.M. Zhai, X.H. Ouyang, H.B. Liu, Effects of different types of biochar on the anaerobic digestion of chicken manure, Bioresour. Technol. 275 (2019) 258–265, https://doi.org/10.1016/j.biortech.2018.12.068.
- [33] P.X. Yan, Y.B. Zhao, H. Zhang, S.S. Chen, W.B. Zhu, X.F. Yuan, Z.J. Cui, A comparison and evaluation of the effects of biochar on the anaerobic digestion of excess and anaerobic sludge, Sci. Total Environ. 736 (2020), 139159, https:// doi.org/10.1016/j.scitotenv.2020.139159.
- [34] Y. Zhao, J.W. Wu, X.F. Yuan, W.B. Zhu, X.F. Wang, X. Cheng, Z.J. Cui, The effect of mixing intensity on the performance and microbial dynamics of a single vertical reactor integrating acidogenic and methanogenic phases in lignocellulosic biomass digestion, Bioresour. Technol. 238 (2017) 542–551, https://doi.org/10.1016/j.biortech.2017.04.080.
- [35] Y. Qin, H.S. Wang, X.R. Li, J.J. Cheng, W.X. Wu, Improving methane yield from organic fraction of municipal solid waste (OFMSW) with magnetic rice-straw biochar, Bioresour. Technol. 245 (2017) 1058–1066, https://doi.org/10.1016/j. biortech.2017.09.047.
- [36] M.W. Wang, Z.Q. Zhao, Y.B. Zhang, Magnetite-contained biochar derived from fenton sludge modulated electron transfer of microorganisms in anaerobic digestion, J. Hazard. Mater. 403 (2021), 123972, https://doi.org/10.1016/j. jhazmat.2020.123972.
- [37] Y. Dong, R.A. Sanford, Y.J. Chang, M.J. Mcinerney, B.W. Fouke, Hematite reduction buffers acid generation and enhances nutrient uptake by a fermentative iron reducing bacterium, orenia metallireducens strain Z6, Environ. Sci. Technol. 51 (2017) 232–242, https://doi.org/10.1021/acs.est.6b04126.
- [38] C.Cruz Viggi, S. Rossetti, S. Fazi, P. Paiano, M. Majone, F. Aulenta, Magnetite particles triggering a faster and more robust syntrophic pathway of methanogenic propionate degradation, Environ. Sci. Technol. 48 (2014) 7536–7543, https:// doi.org/10.1021/es5016789.
- [39] T. Tian, S. Qiao, X. Li, M.J. Zhang, J.T. Zhou, Nano-graphene induced positive effects on methanogenesis in anaerobic digestion, Bioresour. Technol. 224 (2017) 41–47, https://doi.org/10.1016/j.biortech.2016.10.058.
- [40] I. Covarrubias-Garcia, G. Quijano, A. Aizpuru, J.L. Sanchez-Garcia, J. L. Rodriguez-Lopez, S. Arriaga, Reduced graphene oxide decorated with magnetite nanoparticles enhance biomethane enrichment, J. Hazard. Mater. 397 (2020), 122760, https://doi.org/10.1016/j.jhazmat.2020.122760.
- [41] T.W.M. Amen, O. Eljamal, A.M.E. Khalil, N. Matsunaga, Evaluation of nano zero valent iron effects on fermentation of municipal anaerobic sludge and inducing biogas production, IOP Conf. Ser.: Earth Environ. Sci. 67 (2017), https://doi.org/ 10.1088/1755-1315/67/1/012004.
- [42] T.T. Jia, Z.Z. Wang, H.Q. Shan, Y.F. Liu, L. Gong, Effect of nanoscale zero-valent iron on sludge anaerobic digestion, Resources, Conservation and Recycling. 127 (2017) 190–195, https://doi.org/10.1016/j.resconrec.2017.09.007.
- [43] L.H. Su, X.L. Shi, G.Z. Guo, A.H. Zhao, Y.C. Zhao, Stabilization of sewage sludge in the presence of nanoscale zero-valent iron (nZVI): abatement of odor and improvement of biogas production, J. Mater. Cycle. Waste Manage. 15 (2013) 461–468, https://doi.org/10.1007/s10163-013-0150-9.
- [44] R.M. Wang, C.X. Li, N. Lv, X.F. Pan, G.J. Cai, J. Ning, G.F. Zhu, Deeper insights into effect of activated carbon and nano-zero-valent iron addition on acidogenesis and whole anaerobic digestion, Bioresour. Technol. 324 (2021), 124671, https:// doi.org/10.1016/j.biortech.2021.124671.
- [45] P.L. Wang, X.N. Li, Y. Li, Y.L. Su, D. Wu, B. Xie, Enhanced anaerobic digestion performance of food waste by zero-valent iron and iron oxides nanoparticles: comparative analyses of microbial community and metabolism, Bioresour. Technol. 371 (2023), 128633, https://doi.org/10.1016/j.biortech.2023.128633.
- [46] P. Wang, X.T. Chen, X.F. Liang, M.M. Cheng, L.H. Ren, Effects of nanoscale zerovalent iron on the performance and the fate of antibiotic resistance genes during thermophilic and mesophilic anaerobic digestion of food waste, Bioresour. Technol. 293 (2019), 122092, https://doi.org/10.1016/j.biortech.2019.122092.
- [47] E. Abdelsalam, M. Samer, Y.A. Attia, M.A. Abdel-Hadi, H.E. Hassan, Y. Badr, Influence of zero valent iron nanoparticles and magnetic iron oxide nanoparticles on biogas and methane production from anaerobic digestion of manure, Energy. 120 (2017) 842–853, https://doi.org/10.1016/j.energy.2016.11.137.
- [48] A. Hassanein, S. Lansing, R. Tikekar, Impact of metal nanoparticles on biogas production from poultry litter, Bioresour. Technol.. 275 (2018), https://doi.org/ 10.1016/j.biortech.2018.12.048.
- [50] Z.S. Zhang, L. Guo, Y. Wang, Y.G. Zhao, Z.L. She, M.C. Gao, Y.D. Guo, Application of iron oxide (Fe₃O₄) nanoparticles during the two-stage anaerobic digestion with waste sludge: impact on the biogas production and the substrate metabolism, Renew. Energy 146 (2020) 2724–2735, https://doi.org/10.1016/j. renene.2019.08.078.
- [51] A.A. Noonari, R.B. Mahar, A.R. Sahito, K.M. Brohi, Anaerobic co-digestion of canola straw and banana plant wastes with buffalo dung: effect of Fe₃O₄ nanoparticles on methane yield, Renew. Energy 133 (2019) 1046–1054, https:// doi.org/10.1016/j.renene.2018.10.113.
- [52] A.A. Ajayi-Banji, S. Rahman, Efficacy of magnetite (Fe₃O₄) nanoparticles for enhancing solid-state anaerobic co-digestion: focus on reactor performance and retention time, Bioresour. Technol. 324 (2021), 124670, https://doi.org/ 10.1016/j.biortech.2021.124670.

- [53] C. Herrmann, E. Sanchez, M. Schultze, R. Borja, Comparative effect of biochar and activated carbon addition on the mesophilic anaerobic digestion of piggery waste in batch mode, J. Environ. Sci. Health A Tox. Hazard. Subst. Environ. Eng. 56 (2021) 946–952, https://doi.org/10.1080/10934529.2021.1944833.
- [54] E.Y. Lim, H.L. Tian, Y.Y. Chen, K.W. Ni, J.X. Zhang, Y.W. Tong, Methanogenic pathway and microbial succession during start-up and stabilization of thermophilic food waste anaerobic digestion with biochar, Bioresour. Technol. 314 (2020), 123751, https://doi.org/10.1016/j.biortech.2020.123751.
- [55] D.Y. Li, M.Y. Sun, J.F. Xu, T.C. Gong, M.Y. Ye, Y. Xiao, T.X. Yang, Effect of biochar derived from biogas residue on methane production during dry anaerobic fermentation of kitchen waste, Waste Manage. 149 (2022) 70–78, https://doi. org/10.1016/j.wasman.2022.06.006.
- [56] Q.Y. Xu, Y.Q. Liao, E. Cho, J.H. Ko, Effects of biochar addition on the anaerobic digestion of carbohydrate-rich, protein-rich, and lipid-rich substrates, J. Air Waste Manage. Assoc. 70 (2020) 455–467, https://doi.org/10.1080/ 10962247.2020.1733133.
- [57] Y.X. Cui, F.J. Mao, J.X. Zhang, Y.L. He, Y.W. Tong, Y.H. Peng, Biochar enhanced high-solid mesophilic anaerobic digestion of food waste: cell viability and methanogenic pathways, Chemosphere 272 (2021), https://doi.org/10.1016/j. chemosphere.2021.129863.
- [58] S. You, W. Li, W. Zhang, H. Lim, H.W. Kua, Y.-K. Park, A.D. Igalavithana, Y.S. Ok, Energy, economic, and environmental impacts of sustainable biochar systems in rural China, Crit. Rev. Environ. Sci. Technol. 52 (2020) 1063–1091, https://doi. org/10.1080/10643389.2020.1848170.
- [59] P. Li, Q. Wang, X. He, R. Yu, C. He, D. Shen, Y. Jiao, Investigation on the effect of different additives on anaerobic co-digestion of corn straw and sewage sludge: comparison of biochar, Fe3O4, and magnetic biochar, Bioresour. Technol. 345 (2022), https://doi.org/10.1016/j.biortech.2021.126532.
- [60] Y. Jiang, E. Mcadam, Y. Zhang, S. Heaven, C. Banks, P. Longhurst, Ammonia inhibition and toxicity in anaerobic digestion: a critical review, J. Water Process Eng. 32 (2019), https://doi.org/10.1016/j.jwpe.2019.100899.
- [61] T.W.M. Amen, O. Eljamal, A.M.E. Khalil, N. Matsunaga, Biochemical methane potential enhancement of domestic sludge digestion by adding pristine iron nanoparticles and iron nanoparticles coated zeolite compositions, J. Environ. Chem. Eng. 5 (2017) 5002–5013, https://doi.org/10.1016/j.jece.2017.09.030.
- [62] J.B. Liu, J.X. Zheng, Y.T. Niu, Z. Zuo, J.Y. Zhang, Y.S. Wei, Effect of zero-valent iron combined with carbon-based materials on the mitigation of ammonia inhibition during anaerobic digestion, Bioresour. Technol. 311 (2020), 123503, https://doi.org/10.1016/j.biortech.2020.123503.
- [63] D.J. Zhang, P. Lu, M.J. Zhang, Y.D. Wei, J.R. Liang, L.X. Zhou, Elucidating interactive effects of sulfidated nanoscale zero-valent iron and ammonia on anaerobic digestion of food waste, J. Biosci. Bioeng. 135 (2023) 63–70, https:// doi.org/10.1016/j.jbiosc.2022.10.003.
- [64] P. Sharma, U. Melkania, Biochar-enhanced hydrogen production from organic fraction of municipal solid waste using co-culture of Enterobacter aerogenes and E. coli, Int J. Hydrogen. Energy 42 (2017) 18865–18874, https://doi.org/ 10.1016/j.ijhydene.2017.06.171.
- [65] W.W. Yan, D. Lu, J.B. Liu, Y. Zhou, The interactive effects of ammonia and carbon nanotube on anaerobic digestion, Chem. Eng. J. 372 (2019) 332–340, https://doi. org/10.1016/j.cej.2019.04.163.
- [66] Y.F. Deng, J. Xia, R. Zhao, J.X. Xu, X.Y. Liu, Iron-coated biochar alleviates acid accumulation and improves methane production under ammonium enrichment conditions, Sci. Total Environ. 809 (2022), 151154, https://doi.org/10.1016/j. scitotenv.2021.151154.
- [67] F. Lü, C.H. Luo, L.M. Shao, P.J. He, Biochar alleviates combined stress of ammonium and acids by firstly enriching Methanosaeta and then Methanosarcina, Water Res. 90 (2016) 34–43, https://doi.org/10.1016/j. watres.2015.12.029.
- [68] S. Kizito, S.B. Wu, W. Kipkemoi Kirui, M. Lei, Q.M. Lu, H. Bah, R.J. Dong, Evaluation of slow pyrolyzed wood and rice husks biochar for adsorption of ammonium nitrogen from piggery manure anaerobic digestate slurry, Sci. Total Environ. 505 (2015) 102–112, https://doi.org/10.1016/j.scitotenv.2014.09.096.
- [69] M. Zhang, Y. Wang, Impact of biochar supported nano zero-valent iron on anaerobic co-digestion of sewage sludge and food waste: methane production, performance stability and microbial community structure, Bioresour. Technol. 340 (2021), https://doi.org/10.1016/j.biortech.2021.125715.
- [70] L. Di, Q.G. Zhang, F. Wang, H. Wang, H.K. Liu, W.M. Yi, Z.P. Zhang, D.L. Zhang, Effect of nano-Fe₂O₄ biochar on anaerobic digestion of chicken manure under high ammonia nitrogen concentration, J. Clean. Prod. 375 (2022), https://doi. org/10.1016/j.jclepro.2022.134107.
- [71] Z.F. Ning, B. Xu, W.Z. Zhong, C. Liu, X. Qin, W.B. Feng, L. Zhu, Preparation of phosphoric acid modified antibiotic mycelial residues biochar: loading of nano zero-valent iron and promotion on biogas production, Bioresour. Technol. 348 (2022), 126801, https://doi.org/10.1016/j.biortech.2022.126801.
- [72] C.Y. Su, A.F. Tao, L.J. Zhao, P.F. Wang, A.L. Wang, X. Huang, M.L. Chen, Roles of modified biochar in the performance, sludge characteristics, and microbial community features of anaerobic reactor for treatment food waste, Sci. Total Environ. 770 (2021), https://doi.org/10.1016/j.scitotenv.2020.144668.
- [73] Z.G. Liu, Y.W. Xue, F. Gao, X.R. Cheng, K. Yang, Removal of ammonium from aqueous solutions using alkali-modified biochars, Chem. Speciation Bioavailability 28 (2016) 26–32, https://doi.org/10.1080/ 09542299.2016.1142833.
- [74] J. Zhou, X. You, T. Jia, B. Niu, L. Gong, X. Yang, Y. Zhou, Effect of nanoscale zerovalent iron on the change of sludge anaerobic digestion process, Environ. Technol. 41 (2019) 3199–3209, https://doi.org/10.1080/ 09593330.2019.1604811.

- [75] W. Yan, M. Mukherjee, Y. Zhou, Direct interspecies electron transfer (DIET) can be suppressed under ammonia-stressed condition – Reevaluate the role of conductive materials, Water Res. 183 (2020), https://doi.org/10.1016/j. watres.2020.116094.
- [76] Y. Shen, J.L. Linville, P.a.A. Ignacio-De Leon, R.P. Schoene, M. Urgun-Demirtas, Towards a sustainable paradigm of waste-to-energy process: enhanced anaerobic digestion of sludge with woody biochar, J. Clean. Prod. 135 (2016) 1054–1064, https://doi.org/10.1016/j.jclepro.2016.06.144.
- [77] G.J. Wang, Q. Li, X. Gao, X.C.C. Wang, Sawdust-derived biochar much mitigates VFAs accumulation and improves microbial activities to enhance methane production in thermophilic anaerobic digestion, ACS Sustain. Chem. Eng. 7 (2018) 2141–2150, https://doi.org/10.1021/acssuschemeng.8b04789.
- [78] S. R, T.N. Vasa, P.C. Sabumon, A mini review on effect of nano particles of Fe in the anaerobic digestion of waste activated sludge, Mater. Today: Proc. 51 (2022) 1482–1488, https://doi.org/10.1016/j.matpr.2021.10.265.
- [79] A. Mostafa, S. Im, Y.C. Song, S. Kang, D.H. Kim, Enhanced anaerobic digestion of long chain fatty acid by adding magnetite and carbon nanotubes, microorganisms. 8 (2020), https://doi.org/10.3390/microorganisms8030333.
- [80] L. Li, X. Zhang, P. Zhu, X. Yong, Y. Wang, W. An, H. Jia, J. Zhou, Enhancing biomethane production and pyrene biodegradation by addition of bio-nano FeS or magnetic carbon during sludge anaerobic digestion, Environ. Technol. 42 (2020) 3496–3507, https://doi.org/10.1080/09593330.2020.1733674.
- [81] I. Ramos, M. Fdz-Polanco, Microaerobic control of biogas sulphide content during sewage sludge digestion by using biogas production and hydrogen sulphide concentration, Chem. Eng. J. 250 (2014) 303–311, https://doi.org/10.1016/j. cej.2014.04.027.
- [82] H. Jung, D. Kim, H. Choi, C. Lee, A review of technologies for in-situ sulfide control in anaerobic digestion, Renew. Sustain. Energy Rev. 157 (2022), https:// doi.org/10.1016/j.rser.2021.112068.
- [83] M. Farghali, F.J. Andriamanohiarisoamanana, M.M. Ahmed, S. Kotb, T. Yamashiro, M. Iwasaki, K. Umetsu, Impacts of iron oxide and titanium dioxide nanoparticles on biogas production: hydrogen sulfide mitigation, process stability, and prospective challenges, J. Environ. Manage. 240 (2019) 160–167, https://doi.org/10.1016/j.jenvman.2019.03.089.
- [84] L.H. Su, G.Y. Zhen, L.J. Zhang, Y.C. Zhao, D.J. Niu, X.L. Chai, The use of the coreshell structure of zero-valent iron nanoparticles (NZVI) for long-term removal of sulphide in sludge during anaerobic digestion, Environ. Sci. Process Impacts 17 (2015) 2013–2021, https://doi.org/10.1039/c5em00470e.
- [85] L.H. Su, Y.C. Zhao, Chemical reduction of odour in fresh sewage sludge in the presence of ferric hydroxide, Environ. Technol. 34 (2013) 165–172, https://doi. org/10.1080/09593330.2012.689362.
- [86] M. Farghali, F.J. Andriamanohiarisoamanana, M.M. Ahmed, S. Kotb, Y. Yamamoto, M. Iwasaki, T. Yamashiro, K. Umetsu, Prospects for biogas production and H₂S control from the anaerobic digestion of cattle manure: the influence of microscale waste iron powder and iron oxide nanoparticles, Waste Manage. 101 (2020) 141–149, https://doi.org/10.1016/j.wasman.2019.10.003.
- [87] L. Zhang, P. De Schryver, B. De Gusseme, W. De Muynck, N. Boon, W. Verstraete, Chemical and biological technologies for hydrogen sulfide emission control in sewer systems: a review, Water Res. 42 (2008) 1–12, https://doi.org/10.1016/j. watres.2007.07.013.
- [88] P.S. Humbert, J. Castro-Gomes, CO2 activated steel slag-based materials: a review, J. Clean. Prod.. 208 (2019) 448–457, https://doi.org/10.1016/j. jclepro.2018.10.058.
- [89] Y.W. Shen, J.L. Linville, M. Urgun-Demirtas, R.P. Schoene, S.W. Snyder, Producing pipeline-quality biomethane via anaerobic digestion of sludge amended with corn stover biochar with in-situ CO₂ removal, Appl. Energy 158 (2015) 300–309, https://doi.org/10.1016/j.apenergy.2015.08.016.
- [90] F.R. Oliveira, K.C. Surendra, D.P. Jaisi, H. Lu, G. Unal-Tosun, S. Sung, S. K. Khanal, Alleviating sulfide toxicity using biochar during anaerobic treatment of sulfate-laden wastewater, Bioresour. Technol. 301 (2020), 122711, https://doi.org/10.1016/j.biortech.2019.122711.
- [91] T.-H. Tsui, L. Zhang, J.X. Zhang, Y.J. Dai, Y.W. Tong, Engineering interface between bioenergy recovery and biogas desulfurization: sustainability interplays of biochar application, Renew. Sustain. Energy Rev. 157 (2022), https://doi.org/ 10.1016/j.rser.2021.112053.
- [92] A. Choudhury, S. Lansing, Biochar addition with Fe impregnation to reduce H₂S production from anaerobic digestion, Bioresour. Technol. 306 (2020), 123121, https://doi.org/10.1016/j.biortech.2020.123121.
- [93] J. Liu, Y. Ding, W. Qiu, Q. Cheng, C. Xu, G. Fan, G. Song, B. Xiao, Enhancing anaerobic digestion of sulphate wastewater by adding nano-zero valent iron, Environ. Technol. 44 (2022) 3988–3996, https://doi.org/10.1080/ 09593330.2022.2077137.
- [94] J. Zhang, Z. Wang, T. Lu, J. Liu, Y. Wang, P. Shen, Y. Wei, Response and mechanisms of the performance and fate of antibiotic resistance genes to nanomagnetite during anaerobic digestion of swine manure, J. Hazard. Mater. 366 (2019) 192–201, https://doi.org/10.1016/j.jhazmat.2018.11.106.
- [95] Y. Liang, L. Qiu, X. Guo, J. Pan, W. Lu, Y. Ge, Start-up Performance of Chicken Manure Anaerobic Digesters Amended with Biochar and Operated at Different Temperatures, Nat. Environ. Polution Technol. 16 (2017).
- [96] R. Barrena, J. Moral-Vico, X. Font, A. Sánchez, Enhancement of Anaerobic Digestion with Nanomaterials: a Mini Review, Energies. 15 (2022), https://doi. org/10.3390/en15145087.
- [97] E. Casals, R. Barrena, A. García, E. González, L. Delgado, M. Busquets-Fité, X. Font, J. Arbiol, P. Glatzel, K.O. Kvashnina, A. Sánchez, V.F. Puntes, Programmed iron oxide nanoparticles disintegration in anaerobic digesters boosts

biogas production, Small 10 (14) (2014), https://doi.org/10.1002/ smll.201303703, 2801-2808, 2741.

- [98] S.H. Xie, X. Li, C.D. Wang, J. Kulandaivelu, G.M. Jiang, Enhanced anaerobic digestion of primary sludge with additives: performance and mechanisms, Bioresour. Technol. 316 (2020), 123970, https://doi.org/10.1016/j. biortech.2020.123970.
- [99] M. Kaur, P.C. Sahoo, M. Kumar, S. Sachdeva, S.K. Puri, Effect of metal nanoparticles on microbial community shift and syntrophic metabolism during anaerobic digestion of Azolla microphylla, J. Environ. Chem. Eng. 9 (2021), https://doi.org/10.1016/j.jece.2021.105841.
- [100] M.A. Abdel-Rahman, Y. Tashiro, T. Zendo, K. Shibata, K. Sonomoto, Isolation and characterisation of lactic acid bacterium for effective fermentation of cellobiose into optically pure homo L-(+)-lactic acid, Appl. Microbiol. Biotechnol. 89 (2011) 1039–1049, https://doi.org/10.1007/s00253-010-2986-4.
- [101] J. Qiao, Z. Tan, M. Wang, Potential and existing mechanisms of enteric methane production in ruminants, Sci. Agric. 71 (2014) 430–440, https://doi.org/ 10.1590/0103-9016-2013-0423.
- [102] J. Zhou, H. Zhang, J. Liu, L. Gong, X. Yang, T. Zuo, Y. Zhou, J. Wang, X. You, Q. Jia, L. Wang, Effects of Fe(3)O(4) nanoparticles on anaerobic digestion enzymes and microbial community of sludge, Environ. Technol. 44 (2023) 68–81, https://doi.org/10.1080/09593330.2021.1963324.
- [103] G. Yang, C. Xu, S. Varjani, Y. Zhou, J. Wc Wong, G. Duan, Metagenomic insights into improving mechanisms of Fe(0) nanoparticles on volatile fatty acids production from potato peel waste anaerobic fermentation, Bioresour. Technol. 361 (2022), 127703, https://doi.org/10.1016/j.biortech.2022.127703.
- [104] T. Wang, D. Zhang, L. Dai, Y. Chen, X. Dai, Effects of metal nanoparticles on methane production from waste-activated sludge and microorganism community shift in anaerobic granular sludge, Sci. Rep. 6 (2016) 25857, https://doi.org/ 10.1038/srep25857.
- [105] Q. Wang, K. Feng, H. Li, Nano iron materials enhance food waste fermentation, Bioresour. Technol. 315 (2020), 123804, https://doi.org/10.1016/j. biortech.2020.123804.
- [106] J. Tan, J. Wang, J. Xue, S.-Y. Liu, S.-C. Peng, D. Ma, T.-H. Chen, Z. Yue, Methane production and microbial community analysis in the goethite facilitated anaerobic reactors using algal biomass, Fuel 145 (2015) 196–201, https://doi. org/10.1016/j.fuel.2014.12.087.
- [107] A. Pytlak, A. Kasprzycka, A. Szafranek-Nakonieczna, J. Grzadziel, A. Kubaczynski, K. Proc, P. Onopiuk, A. Walkiewicz, C. Polakowski, A. Galazka, J. Lalak-Kanczugowska, Z. Stepniewska, A. Bieganowski, Biochar addition reinforces microbial interspecies cooperation in methanation of sugar beet waste (pulp), Sci. Total Environ. 730 (2020), 138921, https://doi.org/10.1016/j. scitotenv.2020.138921.
- [108] T. Chen, W. Long, C. Zhang, S. Liu, L. Zhao, B.R. Hamaker, Fiber-utilizing capacity varies in Prevotella- versus Bacteroides-dominated gut microbiota, Sci. Rep. 7 (2017) 2594, https://doi.org/10.1038/s41598-017-02995-4.
- [109] G. Martinez-Fernandez, S.E. Denman, C. Yang, J. Cheung, M. Mitsumori, C. S. Mcsweeney, Methane inhibition alters the microbial community, hydrogen flow, and fermentation response in the rumen of cattle, Front Microbiol. 7 (2016) 1122, https://doi.org/10.3389/fmicb.2016.01122.
- [110] N.R. Buan, Methanogens: pushing the boundaries of biology, Emerg. Top. Life Sci. 2 (2018) 629–646, https://doi.org/10.1042/ETLS20180031.
- [111] S. Wang, F. Shi, P. Li, F. Yang, Z. Pei, Q. Yu, X. Zuo, J. Liu, Effects of rice straw biochar on methanogenic bacteria and metabolic function in anaerobic digestion, Sci. Rep. 12 (2022), https://doi.org/10.1038/s41598-022-10682-2.
- [112] G. Wang, P. Fu, B. Zhang, J. Zhang, Q. Huang, G. Yao, Q. Li, M. Dzakpasu, J. Zhang, Y.Y. Li, R. Chen, Biochar facilitates methanogens evolution by enhancing extracellular electron transfer to boost anaerobic digestion of swine manure under ammonia stress, Bioresour. Technol. 388 (2023), 129773, https:// doi.org/10.1016/j.biortech.2023.129773.
- [113] Z. Zhao, Y. Zhang, Q. Yu, Y. Dang, Y. Li, X. Quan, Communities stimulated with ethanol to perform direct interspecies electron transfer for syntrophic metabolism of propionate and butyrate, Water Res. 102 (2016) 475–484, https://doi.org/ 10.1016/j.watres.2016.07.005.
- [114] Y. Cai, X. Shen, X. Meng, Z. Zheng, M. Usman, K. Hu, X. Zhao, Syntrophic consortium with the aid of coconut shell-derived biochar enhances methane recovery from ammonia-inhibited anaerobic digestion, Sci. Total Environ. 872 (2023), 162182, https://doi.org/10.1016/j.scitotenv.2023.162182.
- [115] D. Zhang, Y. Wei, S. Wu, L. Zhou, Consolidation of hydrogenotrophic methanogenesis by sulfidated nanoscale zero-valent iron in the anaerobic digestion of food waste upon ammonia stress, Sci. Total Environ. 822 (2022), 153531, https://doi.org/10.1016/j.scitotenv.2022.153531.
- [116] J. Chen, P. Zhang, J. Zhang, Y. He, Y.W. Tong, Micro–nano magnetite-loaded biochar enhances interspecies electron transfer and viability of functional microorganisms in anaerobic digestion, ACS Sustain. Chem. Eng. 10 (2022) 2811–2821, https://doi.org/10.1021/acssuschemeng.1c08288.
- [117] S. Ren, M. Usman, D.C.W. Tsang, S. OT, I. Angelidaki, X. Zhu, S. Zhang, G. Luo, Hydrochar-facilitated anaerobic digestion: evidence for direct interspecies electron transfer mediated through surface oxygen-containing functional groups, Environ. Sci. Technol. 54 (2020) 5755–5766, https://doi.org/10.1021/acs. est.0c00112.
- [118] E.Y. Lim, J.T.E. Lee, L. Zhang, H. Tian, K.C. Ong, Z.K. Tio, J. Zhang, Y.W. Tong, Abrogating the inhibitory effects of volatile fatty acids and ammonia in overloaded food waste anaerobic digesters via the supplementation of nano-zero valent iron modified biochar, Sci. Total Environ. 817 (2022), 152968, https://doi. org/10.1016/j.scitotenv.2022.152968.

- [119] X. Wang, P. Wang, X. Meng, L. Ren, Performance and metagenomics analysis of anaerobic digestion of food waste with adding biochar supported nano zerovalent iron under mesophilic and thermophilic condition, Sci. Total Environ. 820 (2022), 153244, https://doi.org/10.1016/j.scitotenv.2022.153244.
- [120] P. Antwi, J. Li, P.O. Boadi, J. Meng, E. Shi, X. Chi, K. Deng, F. Ayivi, Dosing effect of zero valent iron (ZVI) on biomethanation and microbial community distribution as revealed by 16S rRNA high-throughput sequencing, Int. Biodeterior. Biodegradation. 123 (2017) 191–199, https://doi.org/10.1016/j. ibiod.2017.06.022.
- [121] L. Zhang, E.Y. Lim, K.-C. Loh, Y.S. Ok, J.T.E. Lee, Y. Shen, C.-H. Wang, Y. Dai, Y. W. Tong, Biochar enhanced thermophilic anaerobic digestion of food waste: focusing on biochar particle size, microbial community analysis and pilot-scale application, energy conversion and management. 209 (2020), https://doi.org/10.1016/j.enconman.2020.112654.
- [122] P. Wang, M. Yu, P. Lin, Y. Zheng, L. Ren, Effects of biochar supported nano zerovalent iron with different carbon/iron ratios on two-phase anaerobic digestion of food waste, Bioresour. Technol. 382 (2023), 129158, https://doi.org/10.1016/j. biortech.2023.129158.
- [123] S.S. Kumar, P. Ghosh, N. Kataria, D. Kumar, S. Thakur, D. Pathania, V. Kumar, M. Nasrullah, L. Singh, The role of conductive nanoparticles in anaerobic digestion: mechanism, current status and future perspectives, Chemosphere 280 (2021), 130601, https://doi.org/10.1016/j.chemosphere.2021.130601.
- [124] R.B. Jeyakumar, G.S. Vincent, Recent advances and perspectives of nanotechnology in anaerobic digestion: a new paradigm towards sludge biodegradability, Sustainability 14 (2022), https://doi.org/10.3390/ su14127191.
- [125] Y. Wu, S. Wang, D.H. Liang, N. Li, Conductive materials in anaerobic digestion: from mechanism to application, Bioresour. Technol. 298 (2020), 122403, https:// doi.org/10.1016/j.biortech.2019.122403.
- [126] F. Liu, A.-E. Rotaru, P.M. Shrestha, N.S. Malvankar, K.P. Nevin, D.R. Lovley, Promoting direct interspecies electron transfer with activated carbon, Energy Environ. Sci. 5 (2012), https://doi.org/10.1039/c2ee22459c.
- [127] A.-E. Rotaru, P.M. Shrestha, F. Liu, B. Markovaite, S. Chen, K.P. Nevin, D. R. Lovley, G. Voordouw, Direct interspecies electron transfer between geobacter metallireducens and methanosarcina barkeri, Appl. Environ. Microbiol. 80 (2014) 4599–4605, https://doi.org/10.1128/aem.00895-14.
- [128] Y.H. Zhu, Z.Q. Zhao, Y.F. Yang, Y.B. Zhang, Dual roles of zero-valent iron in dry anaerobic digestion: enhancing interspecies hydrogen transfer and direct interspecies electron transfer, Waste Manage. 118 (2020) 481–490, https://doi. org/10.1016/j.wasman.2020.09.005.
- [129] H. Li, W.D. Zhang, D. Xia, L.F. Ye, W.D. Ma, H.Y. Li, Q.B. Li, Y.P. Wang, Improved anaerobic degradation of purified terephthalic acid wastewater by adding nanoparticles or co-substrates to facilitate the electron transfer process, Environ. Sci.: Nano 9 (2022) 1011–1024, https://doi.org/10.1039/d1en01037a.
- Sci.: Nano 9 (2022) 1011–1024, https://doi.org/10.1039/d1en01037a.
 [130] J.H. Wu, F.Y. Wu, H.P. Chuang, W.Y. Chen, H.J. Huang, S.H. Chen, W.T. Liu, Community and proteomic analysis of methanogenic consortia degrading terephthalate, Appl. Environ. Microbiol. 79 (2013) 105–112, https://doi.org/10.1128/AEM.02327-12.
- [131] A. Lykidis, C.L. Chen, S.G. Tringe, A.C. Mchardy, A. Copeland, N.C. Kyrpides, P. Hugenholtz, H. Macarie, A. Olmos, O. Monroy, W.T. Liu, Multiple syntrophic interactions in a terephthalate-degrading methanogenic consortium, ISME J. 5 (2011) 122–130, https://doi.org/10.1038/ismej.2010.125.
- [132] L. Chen, Y. Zhang, J. Liang, Y. Li, J. Zhang, W. Fang, P. Zhang, G. Zhang, H. Hao Ngo, Improvement of anaerobic digestion containing sulfur with conductive materials: focusing on recent advances and internal biological mechanisms, Chem. Eng. J. 472 (2023), https://doi.org/10.1016/j.cej.2023.144867.
- [133] G. Zhang, F. Zhang, G. Ding, J. Li, X. Guo, J. Zhu, L. Zhou, S. Cai, X. Liu, Y. Luo, G. Zhang, W. Shi, X. Dong, Acyl homoserine lactone-based quorum sensing in a methanogenic archaeon, ISME J. 6 (2012) 1336–1344, https://doi.org/10.1038/ ismej.2011.203.
- [134] L. Lv, W. Li, Z. Zheng, D. Li, N. Zhang, Exogenous acyl-homoserine lactones adjust community structures of bacteria and methanogens to ameliorate the performance of anaerobic granular sludge, J. Hazard. Mater. 354 (2018) 72–80, https://doi.org/10.1016/j.jhazmat.2018.04.075.
- [135] Y. Zhang, J. Li, F. Liu, H. Yan, J. Li, X. Zhang, A.K. Jha, Specific quorum sensing signal molecules inducing the social behaviors of microbial populations in anaerobic digestion, Bioresour. Technol. 273 (2019) 185–195, https://doi.org/ 10.1016/j.biortech.2018.11.022.
- [136] H. Dang, N. Yu, A. Mou, L. Zhang, B. Guo, Y. Liu, Metagenomic insights into direct interspecies electron transfer and quorum sensing in blackwater anaerobic digestion reactors supplemented with granular activated carbon, Bioresour. Technol. 352 (2022), 127113, https://doi.org/10.1016/j.biortech.2022.127113.
- [137] X. Jing, X. Liu, C. Deng, S. Chen, S. Zhou, Chemical signals stimulate Geobacter soli biofilm formation and electroactivity, Biosens. Bioelectron. 127 (2019) 1–9, https://doi.org/10.1016/j.bios.2018.11.051.
- [138] J.H. Park, J.H. Park, H. Je Seong, W.J. Sul, K.H. Jin, H.D. Park, Metagenomic insight into methanogenic reactors promoting direct interspecies electron transfer via granular activated carbon, Bioresour. Technol. 259 (2018) 414–422, https:// doi.org/10.1016/j.biortech.2018.03.050.
- [139] Q. Yin, K. He, A. Liu, G. Wu, Enhanced system performance by dosing ferroferric oxide during the anaerobic treatment of tryptone-based high-strength wastewater, Appl. Microbiol. Biotechnol. 101 (2017) 3929–3939, https://doi. org/10.1007/s00253-017-8194-8.
- [140] Q. Yin, M. Gu, S.W. Hermanowicz, H. Hu, G. Wu, Potential interactions between syntrophic bacteria and methanogens via type IV pili and quorum-sensing

systems, Environ. Int. 138 (2020), https://doi.org/10.1016/j. envint.2020.105650.

- [141] M. Zhang, Y. Ma, D. Ji, X. Li, J. Zhang, L. Zang, Synergetic promotion of direct interspecies electron transfer for syntrophic metabolism of propionate and butyrate with graphite felt in anaerobic digestion, Bioresour. Technol. 287 (2019), https://doi.org/10.1016/j.biortech.2019.121373.
- [142] R.W. Mckee, N. Aleksanyan, E.M. Garrett, R. Tamayo, Type IV Pili promote clostridium difficile adherence and persistence in a mouse model of infection, Infect. Immun. 86 (2018), https://doi.org/10.1128/iai.00943-00917.
- [143] G.P. Sheng, H.Q. Yu, X.Y. Li, Extracellular polymeric substances (EPS) of microbial aggregates in biological wastewater treatment systems: a review, Biotechnol. Adv. 28 (2010) 882–894, https://doi.org/10.1016/j. biotechady.2010.08.001.
- [144] C.C. Viggi, S. Rossetti, S. Fazi, P. Paiano, M. Majone, F. Aulenta, Magnetite particles triggering a faster and more robust syntrophic pathway of methanogenic propionate degradation, Environ. Sci. Technol. 48 (2014) 7536–7543, https:// doi.org/10.1021/es5016789.
- [145] S. Karri, R. Sierra-Alvarez, J.A. Field, Zero valent iron as an electron-donor for methanogenesis and sulfate reduction in anaerobic sludge, Biotechnol. Bioeng. 92 (2005) 810–819, https://doi.org/10.1002/bit.20623.
- [146] J. Ye, A.D. Hu, G.P. Ren, M. Chen, J.H. Tang, P.Y. Zhang, S.G. Zhou, Z. He, Enhancing sludge methanogenesis with improved redox activity of extracellular polymeric substances by hematite in red mud, Water Res. 134 (2018) 54–62, https://doi.org/10.1016/j.watres.2018.01.062.
- [147] L. Ho, G. Ho, Mitigating ammonia inhibition of thermophilic anaerobic treatment of digested piggery wastewater: use of pH reduction, zeolite, biomass and humic acid, Water Res. 46 (2012) 4339–4350, https://doi.org/10.1016/j. watres.2012.05.016.
- [148] M. Aeschbacher, M. Sander, R.P. Schwarzenbach, Novel electrochemical approach to assess the redox properties of humic substances, Environ. Sci. Technol. 44 (2010) 87–93, https://doi.org/10.1021/es902627p.
- [149] S.C. Khoo, M.S. Goh, A. Alias, V. Luang-In, K.W. Chin, T.H. Ling Michelle, C. Sonne, N.L. Ma, Application of antimicrobial, potential hazard and mitigation plans, Environ. Res. 215 (2022), 114218, https://doi.org/10.1016/j. envres.2022.114218.
- [150] W. Sun, J. Gu, X.J. Wang, X. Qian, X.X. Tuo, Impacts of biochar on the environmental risk of antibiotic resistance genes and mobile genetic elements during anaerobic digestion of cattle farm wastewater, Bioresour. Technol. 256 (2018) 342–349, https://doi.org/10.1016/j.biortech.2018.02.052.
- [151] Y. Bai, R. Xu, Q.P. Wang, Y.R. Zhang, Z.H. Yang, Sludge anaerobic digestion with high concentrations of tetracyclines and sulfonamides: dynamics of microbial communities and change of antibiotic resistance genes, Bioresour. Technol. 276 (2019) 51–59, https://doi.org/10.1016/j.biortech.2018.12.066.
- [152] H.J. Wang, L.Y. Hou, Y.Q. Liu, K.S. Liu, L.P. Zhang, F.Y. Huang, L. Wang, A. Rashid, A.Y. Hu, C.P. Yu, Horizontal and vertical gene transfer drive sediment antibiotic resistome in an urban lagoon system, J. Environ. Sci. (China) 102 (2021) 11–23, https://doi.org/10.1016/j.jes.2020.09.004.

- [153] Z. Tian, Y. Zhang, B. Yu, M. Yang, Changes of resistome, mobilome and potential hosts of antibiotic resistance genes during the transformation of anaerobic digestion from mesophilic to thermophilic, Water Res. 98 (2016) 261–269, https://doi.org/10.1016/j.watres.2016.04.031.
- [154] J.L. Balcazar, How do bacteriophages promote antibiotic resistance in the environment? Clin. Microbiol. Infect. 24 (2018) 447–449, https://doi.org/ 10.1016/j.cmi.2017.10.010.
- [155] M. Pazda, J. Kumirska, P. Stepnowski, E. Mulkiewicz, Antibiotic resistance genes identified in wastewater treatment plant systems - a review, Sci. Total Environ. 697 (2019), 134023, https://doi.org/10.1016/j.scitotenv.2019.134023.
- [156] A. Ezzariai, M. Hafidi, A. Khadra, Q. Aemig, L. El Fels, M. Barret, G. Merlina, D. Patureau, E. Pinelli, Human and veterinary antibiotics during composting of sludge or manure: global perspectives on persistence, degradation, and resistance genes, J. Hazard. Mater. 359 (2018) 465–481, https://doi.org/10.1016/j. jhazmat.2018.07.092.
- [157] P.J. He, Z.F. Yu, L.M. Shao, Y.Z. Zhou, F. Lu, Fate of antibiotics and antibiotic resistance genes in a full-scale restaurant food waste treatment plant: implications of the roles beyond heavy metals and mobile genetic elements, J. Environ. Sci. (China) 85 (2019) 17–34, https://doi.org/10.1016/j.jes.2019.04.004.
- [158] N. Haffiez, T.H. Chung, B.S. Zakaria, M. Shahidi, S. Mezbahuddin, F.I. Hai, B. R. Dhar, A critical review of process parameters influencing the fate of antibiotic resistance genes in the anaerobic digestion of organic waste, Bioresour. Technol. 354 (2022), 127189, https://doi.org/10.1016/j.biortech.2022.127189.
- [159] J.Y. Ma, J. Gu, X.J. Wang, H.L. Peng, Q.Z. Wang, R.R. Zhang, T. Hu, J.F. Bao, Effects of nano-zerovalent iron on antibiotic resistance genes during the anaerobic digestion of cattle manure, Bioresour. Technol. 289 (2019), 121688, https://doi. org/10.1016/j.biortech.2019.121688.
- [160] J.Q. Liao, Y.G. Chen, Removal of intl1 and associated antibiotics resistant genes in water, sewage sludge and livestock manure treatments, Rev. Environ. Sci. Bio/ Technol. 17 (2018) 471–500, https://doi.org/10.1007/s11157-018-9469-y.
- [161] T.T. Lu, J.Y. Zhang, T.M. Su, X.L. Liang, Y.S. Wei, T.G. He, Coupled mechanism of enhanced and inhibitory effects of nanoscale zero-valent iron on methane production and antibiotic resistance genes in anaerobic digestion of swine manure, Bioresour. Technol. 360 (2022), 127635, https://doi.org/10.1016/j. biortech.2022.127635.
- [162] Y. Shuo, C.Z. Qiang, W.Q. Xue, Impacts of biochar on anaerobic digestion of swine manure: methanogenesis and antibiotic resistance genes dissemination, Bioresour. Technol. 324 (2021), https://doi.org/10.1016/j. biortech.2021.124679.
- [163] Y. Li, W.Z. Zhong, Z.F. Ning, J. Feng, J.R. Niu, Z.X. Li, Effect of biochar on antibiotic resistance genes in the anaerobic digestion system of antibiotic mycelial dreg, Bioresour. Technol. 364 (2022), 128052, https://doi.org/10.1016/j. biortech.2022.128052.
- [164] J.Y. Zhang, C. Buhe, D.W. Yu, H. Zhong, Y.S. Wei, Ammonia stress reduces antibiotic efflux but enriches horizontal gene transfer of antibiotic resistance genes in anaerobic digestion, Bioresour. Technol. 295 (2020), 122191, https:// doi.org/10.1016/j.biortech.2019.122191.