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Nanomaterial-enhanced anaerobic digestion for sustainable bioenergy production: opportunities, challenges and territorial issues. A systematic bibliometric review

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ABSTRACT

Anaerobic digestion (AD) is a promising biotechnology for organic waste management, simultaneously contributing to sustainable bioenergy generation. Despite its potential, enhancing methane production and achieving process optimization remain significant challenges. The integration of nanomaterials (NMs) into AD systems has shown promise in enhancing biogas quality and yield, as well as stabilizing the process. Nevertheless, the diversity of NMs (including metallic and carbon-based) applied to various types of organic wastes leads to inconsistent results, highlighting the need for a more comprehensive understanding of the underling biochemical mechanisms when NMs are incorporated. This review examines current research challenges and opportunities related to the application of NMs in the AD processes. Through a systematic literature review, following a protocol for the selection of scientific articles and patents, 46 articles and 36 patents are identified. The majority of relevant studies are concentrated in developed countries, and patent analysis suggests the technology is evolving from the emerging stage to the growth phase, with maturity anticipated by 2037. Metadata analysis reveals that the application of NMs can enhance biogas production by up to 25 % compared to conventional AD processes, with iron-based metallic NMs demonstrating superior methane yield in the treatment of manure, sewage sludge, and lignocellulosic waste. In contrast, carbon-based NMs, while less effective in enhancing biogas yield, also face cost-related barriers that may hinder industrial scalability. This article identified seven key research challenges and opportunities to guide the application of NMs in AD processes and promote their large-scale implementation in waste-to-energy conversion.

Abbreviations

AD	Anaerobic Digestion
BMP	Biochemical Methane Potential
CI	Confidence Intervals
CNTs	Carbon Nanotubes
C/N	Carbon-to-Nitrogen
COD	Chemical Oxygen Demand
CVT	Cumulative Value of Technology
CZVMs	Conductive Zero-Valent Metals
DIET	Direct Interspecies Electron Transfer
EET	Extracellular Electron Transfer
ERL	Expected Remaining Life
GHG	Greenhouse Gases
GO	Graphene Oxide

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LCA	Life Cycle Assessment
MCA	Multiple Correspondence Analysis
MCR	Methyl-Coenzyme M Reductase
MSE	Mean Square Error
R&D	Research and Development
SRB	Sulfate-Reducing Bacteria
TLC	Technology Life Cycle
TMR	Technology Maturity Ratio
TSS	Total Suspended Solids
PPA	Predicted Number of Patents
NM	Nanomaterial
VFA	Volatile Fatty Acids
WWTP	Wastewater Treatment Plant
ZVI	Zero-Valent Iron

1. Introduction

The rapid growth in global population, industrialization, and consumer demand for goods and services has significantly increased the need for energy, which is predominantly supplied by non-renewable energy sources such as oil, coal, and natural gas [1]. According to Dikshit et al. [2], approximately 88 % of the world's energy is derived from non-renewable sources. The extensive use of fossil fuels has led to substantial greenhouse gases (GHG) emissions, contributing to climate change and environmental degradation [3]. This has created an urgent need for alternative energy sources to reduce reliance on fossil fuels, supporting sustainable development in modern societies [4].

Renewable energy sources like wind, hydroelectric, solar, and biomass energy are increasingly being explored as viable alternatives [2]. Among these, biomass holds particular promise, as it can be transformed into biofuels, biodiesel, bioethanol, bioelectricity, and biogas through various conversion technologies [5,6]. Specifically, anaerobic digestion (AD) presents unique advantages by simultaneously addressing organic waste management and clean energy generation. Unlike solar, wind, or hydroelectric systems, AD utilizes biodegradable feedstocks such as agricultural residues, food waste, and animal manure to produce biogas and nutrient-rich digestate, thereby contributing to both energy and soil fertility systems. This dual functionality enables circular resource use and significantly reduces greenhouse gas emissions through methane capture and fossil fuel substitution [7]. Furthermore, AD systems are scalable, from rural household digesters to centralized industrial facilities, making them accessible to off-grid communities and aligned with decentralized energy models. Importantly, AD contributes directly to multiple United Nations Sustainable Development Goals (SDGs), including SDG 2 (Zero Hunger), SDG 6 (Clean Water and Sanitation), SDG 7 (Affordable and Clean Energy), SDG 11 (Sustainable Cities and Communities), SDG 12 (Responsible Consumption and Production), and SDG 13 (Climate Action). Its indirect benefits extend to SDG 1 (No Poverty), SDG 3 (Good Health and Well-being), and SDG 8 (Decent Work and Economic Growth), reinforcing its role as a critical technology in achieving a sustainable and inclusive bioeconomy [8,9].

AD is a biological process in which organic waste is decomposed through the action of microorganisms in the absence of oxygen, producing biogas primarily composed of methane (CH_4), carbon dioxide (CO_2), and traces of hydrogen sulfide (H_2S) [10]. The efficiency of AD depends on various factors, including substrate pH, carbon-to-nitrogen (C/N) ratio, temperature, and hydraulic retention time.

To optimize AD, researchers have experimented with various additives and inoculants, such as microbes, enzymes, biological metabolites, anti-foaming agents, activated carbon, graphite, chelating agents, and nanoparticles, to enhance biomethane production [3]. These additives play a critical role in supporting the microbial consortia, particularly by promoting biofilm formation and facilitating electron transfer between species [11], which are crucial for high-quality biogas production [12]. However, cost constraints limit the industrial application of certain additives, as they may not justify their expense or effectively generate value-added products from the AD [3,13]. The most applicable additives are those with reuse potential or produced through biosynthesis processes [14].

Nanomaterial (NM) additives have gained considerable attention for their potential to improve AD process stability and increase biogas quality and yield. NMs are three-dimensional particles, typically 1–100 nm in size [12,15], that can influence biochemical and physicochemical processes within AD (16). Early studies in 2006 examined NM applications in AD of animal manure, but the specific effects on biogas production were not detailed. The first investigation into the impact of particle size of metal oxides (ZnO and CuO) on methane and biogas production in AD was conducted in 2011 [17]. A subsequent study in 2014 examined the application of iron nanoparticles, assessing both their effects on anaerobic processes and their economic feasibility for future large-scale implementation [18].

NMs are generally categorized as metallic nanoparticles, carbon nanotubes, and metal oxides [13]. Their unique characteristics, including high particle concentration per unit weight, high surface-to-volume ratio, and confinement effects, distinguish them from bulk materials of the same composition, imparting distinct properties that can enhance AD performance [19].

The biogas yield and methane purity achieved in AD can vary widely depending on the type of NM used [16]. For example, metallic NMs such as Fe, Ni, Zn, and Mn have positively affected biogas yield and methane content. In contrast, NMs containing Ag and Ti may exhibit antibacterial properties that could inhibit the AD process [20]. Moreover, Tian et al. [21] found that combining metallic NMs (Fe, Ni, Co, Ni) with carbon-based NMs (e.g., activated carbon, graphene, and biochar) can enhance microbial activity across different AD stages. Thus, NMs are excellent electron acceptors or donors across all stages (from hydrogenotrophic bacteria to methanogenic archaea) of the AD process, helping to improve the quality of value-added byproducts (biogas and digestate) [16].

Numerous studies have investigated NM influence on AD. Recent reviews by researchers such as Khan et al. [22], Salehi and Wang [23], Li et al. [24], Ugwu and Enweremadu [25], Jeyakumar and Vincent [26], Hassanein et al. [27], Kong et al. [9], and Zhu et al. [28] analyse NM effects in AD through bibliometric, conceptual, or critical perspectives. These qualitative approaches, however, introduce subjectivity, potentially resulting in data loss. Parra-Orobio et al. [3] recommend systematic and metadata-driven reviews using specialized software to assess the range of variables influencing AD, as non-systematic methods may produce inconsistent findings.

Current research reveals that NM use in AD still requires a deeper understanding of microbial diversity, the biochemical mechanisms that underpin NM interactions, and their impacts on AD biological and chemical reactions [29]. Studies have also investigated iron NM recovery in reactors to reduce NM presence in digestate [29] and identified mechanisms of NM deactivation over time [30], yet further investigation is required to address environmental implications of NMs post-AD. González et al. [31] highlight that while NMs may improve AD efficiency, their potential release into the environment, especially through digestate application to soil, could impact nutrient cycles and biochemical processes.

This article identifies challenges and opportunities for implementing NMs in AD on an industrial scale with economic feasibility in mind. While previous reviews (e.g. Refs. [9,22–28]) focus on specific NMs or AD substrates, this study offers a comprehensive analysis of NM effects in AD, employing statistical tools and models to assess synergistic or antagonistic interactions and evaluate technology maturity. Additionally, it includes a patent review to predict technology performance at full scale. The article concludes with a discussion of challenges and perspectives, providing insights for advancing NM-based AD applications in waste-to-energy conversion.

2. Materials and methods

2.1. Literature search

A systematic literature search was performed using major scientific databases, including Scopus® and Web of Science (WOS)®, with search strings such as "nanoparticles AND anaerobic digestion," "nanomaterials AND organic waste AND anaerobic digestion," "nanoparticles AND lignocellulosic waste AND anaerobic digestion." These databases were selected for their size and recognition in the scientific community [32]. Additionally, a patent analysis was conducted following the guidelines of Sinisterra et al. [33] and Cely-Bautista et al. [34], using the same keywords across Google Patents®, Scopus Patents, and Lens® databases. The data collected was further processed using the free version of the Esp@cenet® software. The search covered scientific articles and patents published between January 2010 and June 2023 to capture current trends in NM-based AD applications. This period was selected as it captures shifts in research trends within a rapidly evolving field and aligns with the timeframes adopted in previous reviews on anaerobic digestion, food waste, and related topics [7,35]. This search retrieved a total of 136 articles and 86 patents.

2.2. Selection criteria

To focus on recent advances in NM applications in the AD of organic waste, a systematic review was conducted following the PRISMA® methodology. PRISMA® provides a structured framework for identifying, selecting, and analysing data from databases [3] and has been previously employed in solid waste management studies [36–38]. Fig. 1 outlines the stages for information retrieval and organization, incorporating three filtering criteria: i) the title or abstract must contain keywords or their variants, specifically "nanoparticles," "nanomaterials," "anaerobic digestion," "organic waste," or "lignocellulosic waste"; ii) the article or patent must present data on NM application in the AD process of organic waste; and iii) publications included must be original research articles, excluding review or conference papers, with no duplicate patents across different databases. Following these criteria, 46 articles were deemed relevant, downloaded in CSV format, and processed using Excel® software [3]. Additionally, 36 patents met the established selection protocols.

2.3. Synthesis and analysis of information (articles and patents)

The consolidated data in CSV format were exported and analysed using the Bibliometrix® tool (University of Naples Federico II in Naples, Italy). Bibliometrix is an open-source R package developed for quantitative research in scientometrics and bibliometrics [38]. Using this tool, insights was obtained on countries with the highest academic productivity, research trends, and thematic maps, which categorized themes into four quadrants: i) driving themes, ii) basic themes, iii) emerging or declining themes, and iv) highly specialized or niche themes [3].

The selected articles were reviewed to extract information on the effects of NM use on variables such as biochemical methane potential (BMP), and the efficiency of reducing chemical oxygen demand (COD), volatile fatty acids (VFAs), and pH levels. These variables were statistically characterized using box plots and frequency analysis in R®, allowing for comparison of NM effects [39]. Additionally, the interquartile range was used to identify any outliers.

For patent analysis, a Technology Life Cycle (TLC) analysis was conducted to assess the advancement stage of the technology. The logistic growth model (Equation (1)) proposed by Sinisterra et al. [33] was applied to represent TLC growth over time, with model fitting performed using Monte Carlo simulations (1000 iterations) to minimize the mean squared error. The simulations were performed using Matlab2022b® software (MathWorks, Inc. Natick, Massachusetts, United States). The model fitting considers patent records from 2011 to 2023, as patents are typically published within 18 months after initial submission [40].

$$Y(t) = \frac{L}{1 + e^{-k(t-t_0)}} \qquad \text{Equation 1}$$

Where *Y(t)* is the dependent variable representing the S-curve; *L* is the

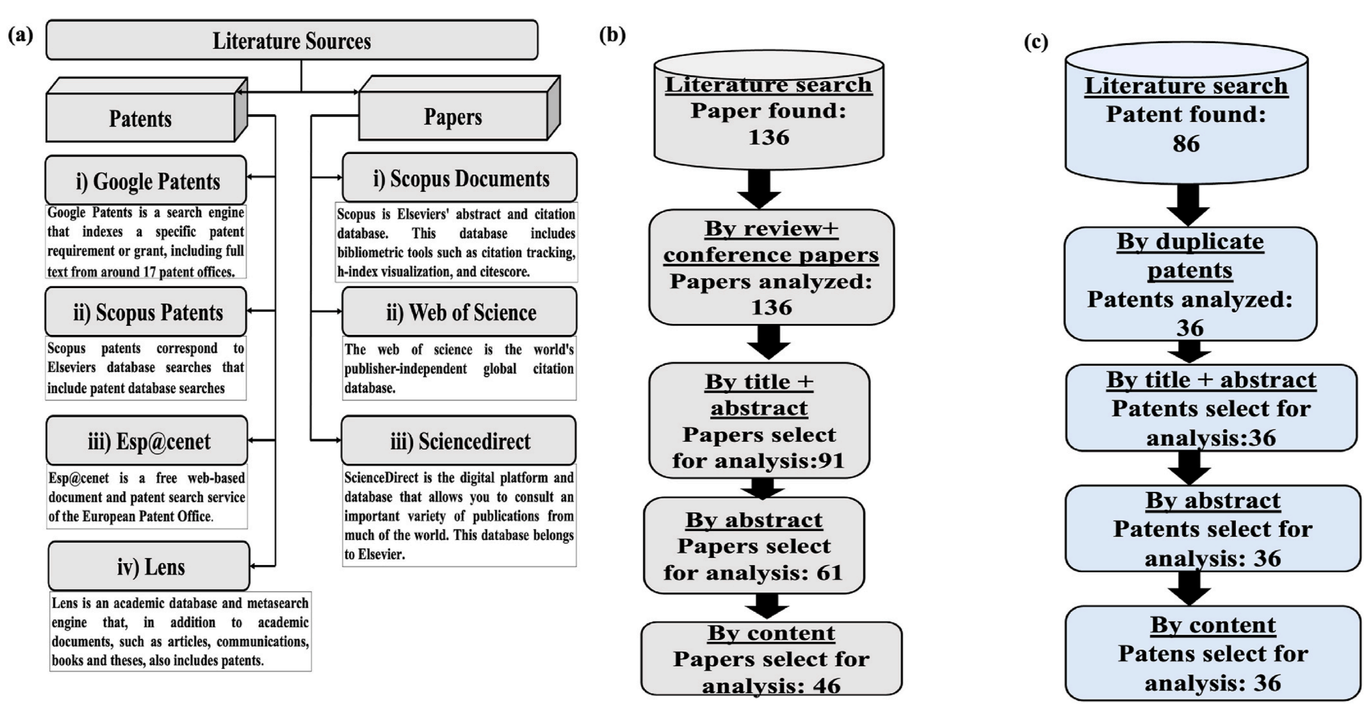

Fig. 1. Overview of the information retrieval and organization stages. (a) Search engines used for quantifying patents and scientific documents published between 2010 and 2023; (b) Selection process for identifying relevant articles on NM application in the AD of organic waste; (c) Selection process for patents related to the use of NMs in AD for organic waste management, detailing the filtering criteria applied and final selection of patents.

asymptotic (maximum) value; and t_0 and k are model parameters automatically defined by the software, representing the midpoint and slope, respectively. Using these parameters, technology indices such as the Technology Maturity Ratio (TMR), Predicted Number of Patents (PPA), and Expected Remaining Life (ERL) were estimated according to Yoon et al. [40]. These indices were calculated with Equations (2) and (3), where TMR (its value ranging from 0 to 1) indicates the proximity of the technology to its maximum development level, and PPA forecasts potential patent registrations:

$$TMR(t) = \frac{L_{now}}{L} \qquad \text{Equation 2}$$

$$PPA(t) = L - L_{now} \qquad \text{Equation 3}$$

Where L_{now} represents the cumulative number of patents at time t. Setting t to a specific year enables estimation of TMR and PPA for that time. For ERL, Equation (4), estimates the remaining lifespan, assuming a threshold ρ where the cumulative patent count reaches of 90 % of L.

$$ERL(t) = T_\rho - t \qquad \text{Equation 4}$$

Where $T\rho$ is the projected year when cumulative patents reach $\rho \times L$. Following Gao et al. [41], the TLC curve indicates the following technology stages: i) emerging stage, with minimal competitive impact; ii) growth stage, marked by high competitiveness without products integration; iii) maturity stage, characterized by competitive impact and product integration; and iv) saturation stage, indicating reduced competitiveness and a shift towards cost reduction [42].

To evaluate the synergistic or antagonistic effect of NM on AD processes, forest plots were created in R® using the "forestplot" package, as recommended by Nigussie et al. [43]. Each box in the diagram represents the average effect size of NM on the examined variables, with horizontal lines indicating 95 % confidence intervals (CIs). The mean effect sizes and CIs were transformed for ease of interpretation, with the percentage change calculated using Equation (5).

$$EB = ([R - 1])*100 \qquad \text{Equation 5}$$

Where EB represents the effect of NMs, and R is the mean effect size after inverse transformation. The effect of the NMs was considered significant if the p-value was <0.05 and if the CIs did not overlap zero. For subgroup analyses, a significant difference was indicated if CIs did not overlap.

3. Results and discussion

3.1. Trends and current status NM applications in AD

Fig. 2 presents the global trends in NM applications in the AD of organic waste, focusing on both academic publications and patent filings between 2011 and 2023 (Table 1-Supplementary). Developed countries dominate this area, producing 57.5 % of the publications and 97.5 % of patents. Notably, China stands out with 29 articles and 17 patents. Cely-Bautista et al. [34] attribute China's significant output to its strategic focus on creating industrial clusters for NM production using low-cost manufacturing. This approach has enabled China to surpass developed countries like the United States, United Kingdom, Germany, and Japan in NM research and technology development. Within European Union, the adoption of NM technologies in AD is expected to increase in alignment with policies supporting renewable energy. This shift has already led to a 30 % rise in methane production via AD, highlighting the EU's commitment to sustainable energy [44]. It is worth highlighting the findings for Canada, where no publications were identified, but patents were (Table 2-Supplementary). This is possibly due to the significant use of nanomaterials in the Canadian market, particularly in the environmental and energy sectors. Moreover, patent holders appear to target markets with strong regulatory frameworks and advanced implementation of this technology, which contrasts with the situation in developing countries.

In contrast, while developing countries contribute 42.5 % of the intellectual output on this topic, they lag behind in patent production, limiting the practical impact of their research. Egypt's progress is particularly noteworthy, as it has recently increased its academic contributions in NM-related AD research. This advancement can likely be attributed to strategic investments made in nanotechnology, which elevated Egypt's rank in the field by 15 places in 2018, positioning it 22nd out of 106 countries [45]. This progress aligns with Egyptian policies aimed at developing alternative energy sources, supporting the country's efforts in sustainable energy initiatives [46].

3.2. Correlations and advances in NM applications in AD

Fig. 3 shows the thematic development and corrections in NM applications within AD of organic waste, with a thematic map (Fig. 3a) and Multiple Correspondence Analysis (MCA) (Fig. 3b). In the thematic map, keywords are categorized by relevance and research maturity. Keywords such as "nanomaterials," "biogas production," "greenhouse gases," and "life cycle analysis" appear as motor themes, indicating well-established, high-impact areas in the field. Notably, while the term "biogas production" is prominent in the MCA, it differs from "methane production," which more directly aligns with energy yield enhancements associated with NM use in AD. Some studies, such as Cerrillo et al. [30], distinguish between biogas production and methane production, the latter of which improves biogas energy content and quality through *in-situ* enhancement.

The MCA further classifies "anaerobic digestion" and "methane production" as basic themes, indicating their foundational importance but highlighting a need for additional research to advance these topics [47]. While some NMs can significantly boost biogas production, other studies report only modest gains, focusing more on methane content [30]. This differentiation between "biogas production" and "methane production" is crucial, as the latter directly impacts energy value. As research on these terms develops, they may evolve into motor themes.

Emerging or declining themes, such as "nanoparticles" and "microbial community analysis", show low density and centrality, suggesting these topics are still relatively underdeveloped. According to López-Robles et al. [48] and Assis and Gonçalves [49], such topics may present cross-cutting themes in AD research but lack novelty. Fig. 3b presents three clusters of NM related variables in AD. The largest cluster (red) centres on NM applications for biogas generation, methane production, biohydrogen, and volatile fatty acids, along with NM-related inhibition processes. This cluster underscores biogas generation as a pivotal variable, highlighting recent advances in the effects of NMs on AD performance and microbial community structure. However, studies on combining NMs to simultaneously enhance biogas quality and yield remain limited [50]. The blue cluster in Fig. 3b focuses on NMs' role in direct interspecies electron transfer (DIET) in AD, a field gaining attention as researchers explore how NMs influence microbial electron exchange [50]. The green cluster emphasizes NMs' impact on greenhouse gas (GHG) emissions, with Hijazi et al. [51] asserting that specific NMs, like cobalt nanoparticles, can notably reduce GHG emissions.

Fig. 4 depicts the evolution of scientific publications and keyword co-occurrence from 2010 to 2023, based on data from WoS® and Scopus®. Larger circles in the cluster map correspond to years with greater publication. At the same time, Fig. 4a highlights that "nanomaterials" and "anaerobic digestion" as consistently dominant terms, particularly in 2021, make a surge in publications. Before 2021, "inhibition," "inhibition constants," and "silver nanoparticles" were prevalent terms. Post-2021, terms such as "biogas," "bioenergy," and "nanomaterials" gained prominence, indicating a shift in focus from AD process challenges to value-added products like biogas and energy. The changing frequency of terms over time reflects an evolving focus on optimizing AD through NMs. Initially, studies concentrated on the AD process itself,

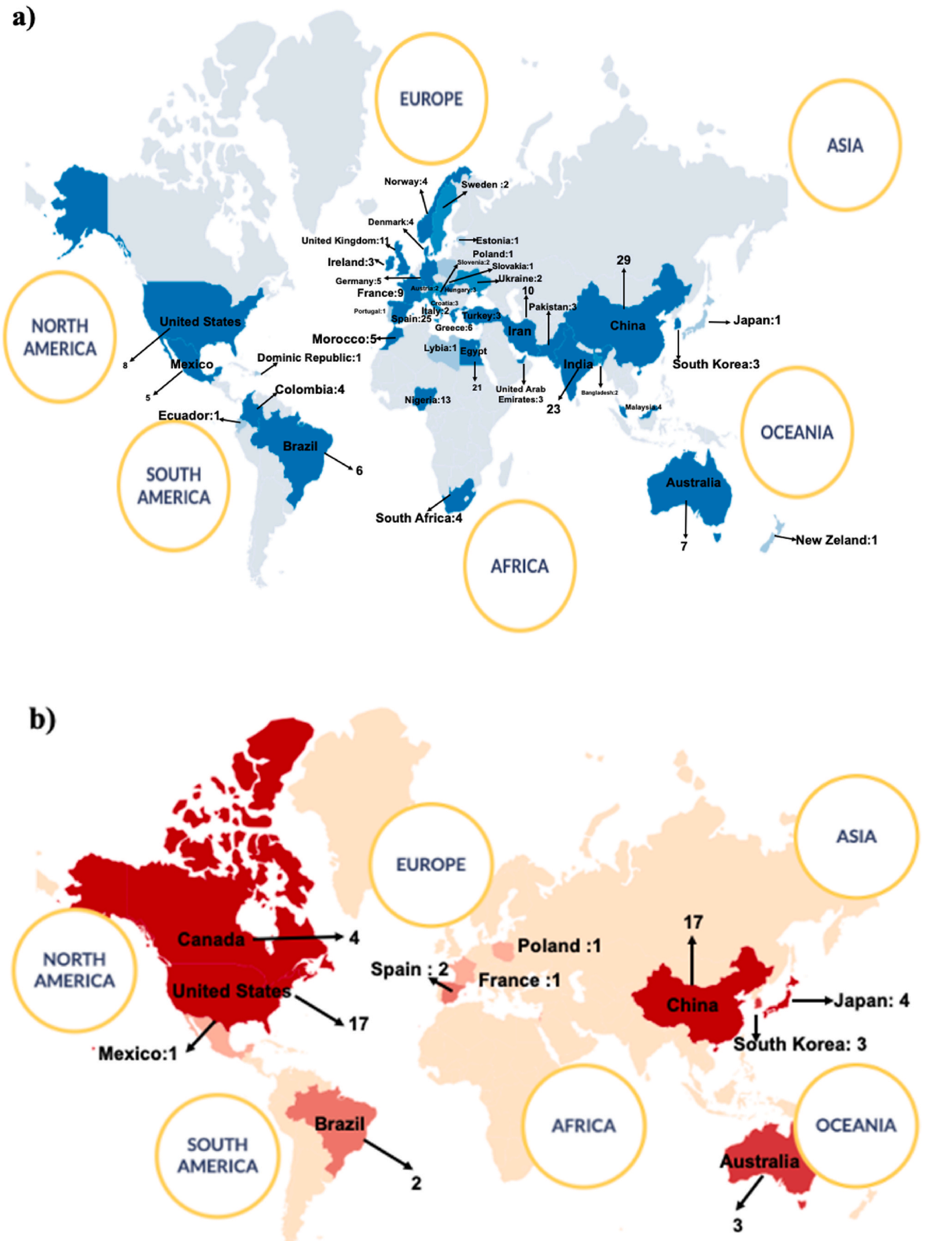

Fig. 2. Global overview of publications and patents related to the applications of NMs in the AD of organic waste. a) Academical article production; b) Patent development.

Table 1
Overview of NM applications in AD and their effects on key response variables.

Waste Type	Inoculum	T (°C)	T. F	Scale	D.E (days)	NM	Dosage	CH_4 production	% COD	VFA (mg/L)	pH	Kinetic study	Source
Primary sludge	WWTP sludge	35	Batch	Laboratory	–	TiO_2/ZnO	0, 6, 30, 150 mg/g TSS	N.R	N.R	N.R	N.R	N.R	[67]
Food waste/Primary sludge	Anaerobic digester sludge	35	Batch	Laboratory	28	Mg	25, 50, 80 mg/L	341, 478, 481	55, 78,80	500, 749, 1214	N.R	Yes (Gompertz)	[68]
Synthetic WW	Brewery WWTP sludge	35/ 35	Batch/ SemicontinuoS	Laboratory	9/30	Fe_3O_4	200 mg/L	128	55	N.R	7.6	No	[69]
Bovine manure	Anaerobic digester sludge	36	Batch	Laboratory	14	ZnO/CuO	57.3 mg/L	101	N.R	N.R	6.9	No	[70]
Secondary sludge	Anaerobic sludge	35	Batch	Laboratory	30	Zn	1000 mg/L	N.R	76.5	1200	7.3	No	[71]
WWTP sludge	Anaerobic sludge	37	Batch	Laboratory	30	Fe	0.1 g/gVS	10.4	66.2	N.R	8.5	No	[72]
Bovine manure	Fresh bovine manure	37	Batch	Laboratory	40	Co, Ni, Fe, Fe_3O_4	1, 2, 20, 20 mg/L	208.9, 304.1, 234.4	N.R	N.R	N.R	No	[12]
Food waste	Manure	37	Batch	Laboratory	59	Fe_3O_4	50, 75, 100, 125 mg/L	136.8, 213.9, 168.5, 84.5	N.R	N.R	6.74–7.11	No	[73]
Buffalo dung/banano waste/canola straw	Buffalo dung	37	Batch	Laboratory	40	Fe_3O_4	81 mg/L	256	–	270	7.1	No	[74]
Saccharose	WWTP sludge	35	Continuous	Laboratory	7.5	Single-walled carbon nanotubes	1000 mg/L	N.R	68.5	100	N.R	Yes (first order)	[75]
Brewery WWTP sludge	Granular sludge	36	Batch	Laboratory	4	Multi-walled carbon nanotubes/ Fe_2O_3	1500, 750 mg/L	10.6, 11.2	97, 96.5	1.9, 2.5	N.R	No	[76]
Glucose	Brewery WWTP sludge	30	Batch	Laboratory	40	CeO_2/ZnO	10, 100, 500, 1000 mg/L	1015.2, 852.6, 594, 542.7/900, 948.8490.5, 146	97.4, 97, 96.7, 96.7/ 97.4, 97.3, 95.7, 38.5	1300, 1100, 1150, 1000/1250, 1250, 1200, 4600	5.9–6.94	No	[77]
Pig manure	Pig manure	35	Batch	Laboratory	30	Fe/Fe_3O_4	20, 10 mg/ L	317.2, 322.9	52.2, 73.9	6690, 6250	7.3–7.4	Yes (first order)	[78]
Secondary sludge	WWTP sludge	35	Batch	Laboratory	50	Fe	2400 mg/L	180	48.6	2340	7.4	No	[79]
Pig manure	WWTP sludge	30	Batch	Laboratory	1.25	Fe	3, 7, 15, 25, 50 mg/L	46.7,48.6, 39.3, 32.4, 14.2	80, 82.5, 85, 89.2, 87.5	N.R	7.6–8.02	No	[80]
Sheep manure	Industrial WWTP sludge	35	Batch	Laboratory	45	Carbon 60/Single-walled carbon nanotubes	50, 500 mg/kg	40, 50/45, 60	N.R	N.R	8.7–8.8	No	[81]
Pig manure	Pig manure	37	Batch	Laboratory	22	Graphene oxide	5, 50, 100, 500 mg/L	250, 260, 280, 240	38.2, 41.1, 42.6, 42.8	400	7.51–7.59	No	[82]
Brewery secondary sludge	Granular sludge	36	Continuous	Laboratory	72	Fe_2O_3/Multi-walled carbon nanotubes	750, 1500 mg/L	8374.9, 7313.2	93, 84	1	N.R	No	[83]
Chicken manure	Chicken Manure digestate	38	Batch	Laboratory	30	Fe_3O_4/carbon nanotubes	3200, 3500	196, 201	N.R	200, 100	N.R	No	[84]
Glucose	Anaerobic digester sludge	35	Batch	Laboratory	8.3	Carbon nanotubes	1000, 3000, 5000 mg/L	144.8, 147.9152.1	N.R	245, 315, 315	N.R	Yes (Gompertz)	[85]

(*continued on next page*)

Table 1 (*continued*)

Waste Type	Inoculum	T (°C)	T. F	Scale	D.E (days)	NM	Dosage	CH_4 production	% COD	VFA (mg/L)	pH	Kinetic study	Source
Okra waste	Food waste digestate	37	Batch	Laboratory	32	Ppy/Fe_3O_4	20, 75, 750, 1000 mg/L	904.45, 887, 830.55, 727.3	N.R	N.R	7.05–7.4	Yes (Gompertz and first order)	[25]
Chicken manure	Chicken Manure digestate	35	Batch	Laboratory	90	Biochar/Fe/ Fe_3O_4	3.3 g/g, 1000, 6000 mg/L	260, 266, 276, 225,288	N.R	1920, 1970, 1470,2170,2020	8.3–8.4	Yes (Gompertz)	[86]
Carbamazepine	Citrus WWTP granular sludge	37	Batch	Laboratory	12	$LaFeO_3$	5, 25, 50, 100, 200	280, 290, 280, 260, 200	N.R	N.R	N.R	Yes (Gompertz)	[87]
WWTP sludge/ Bovine manure	Anaerobic digester sludge	37	Batch	Laboratory	30	Fe_3O_4	40, 80, 120, 160 mg/L	285.4, 328.8, 382.3, 511.2	72.85, 76.78, 81.47, 91.68	200, 180, 100, 100	N.R	Yes (Gompertz)	[88]
Food waste	WWTP sludge	55	Batch	Laboratory	7	Biochar/Fe	120 mg/L	793	68.1	42700	N.R	No	[89]
Bovine manure	Bovine digestate	33	Batch	Laboratory	30	Ni	1,2,4 mg/L	21.81, 31.69, 28.59	N.R	3900, 3600, 4100	6.9–7.0	Yes (Gompertz and first order)	[90]
Glucose	Granular sludge	37	Batch	Laboratory	8	Mg	50, 100, 200, 300, 400, 500 mg/L	160, 165, 180, 160, 160, 158	27.92, 27.92, 30.68, 27.92, 27.92, 27.92	1300, 1300, 900, 1200, 1200, 1200	7.08–7.2	No	[91]
Actived sludge	WWTP sludge	55	Batch	Laboratory	32	Fe	25, 100, 250	4.93, 34.10, 34.43	N.R	6500,2000, 1800	6.5–8.5	No	[92]

Note: WW: wastewater; T: Temperature; T; F: Type of feeding; D.E: Duration of the experiment; T.N: Type of nanomaterial; N.R: Not reported; %COD: COD removal.

while more recent research emphasizes energy outputs and biogas quality. This shift indicates the field's growing interest in enhancing the AD process to achieve sustainable energy production, aligning with emerging environmental and economic priorities.

Fig. 4 (b) presents a network analysis of the 50 most frequently used keywords NM applications in AD from 2011 to 2023. The map organizes keywords into two primary clusters based on relational strength, with a minimum occurrence threshold of 25. between elements, resulting in clusters of closely related elements. The red cluster is centred on AD process variables and the effect of NMs, while the blue cluster emphasizes NM sources, generation, and broader applications. Circle sizes are directly proportional to keyword linkage strength, with "anaerobic digestion" as the central term indicating its broad relevance across studies. In summary, the increased diversity of keywords overtime reflects the expansion of NM applications in AD. The trend is consistent with technology consolidation, as research diversifies into various subtopics, strengthening NM integration into AD for organic waste valorisation [3].

3.3. Technological evolution of NM applications in AD

Fig. 5 presents the CVT analysis of patents associated with NM applications in AD of organic waste, based on a logistic growth model. The model parameters are as follows: midpoint year (t_0) of 2025, growth rate (k) of 0.2, and asymptotic limit (L) of 92 patents, yielding a high fit with $R^2 = 0.987$ and MSE $= 1.254$. This strong model fit confirms the reliability of the predictive analysis for technology development stages and patent growth in NM-related AD applications. Key indices, including TMR, PPA, and ERL, were determined for the end of 2016, offering insight into technology's position in its life cycle.

The TMR for NM applications in AD was approximately 10.85 % in early 2016, with 10 patents registered out of the projected total of 92. This value indicates that approximately 89.15 % of development remains, consistent with the thematic map (Fig. 3a) and trends in scientific output (Fig. 1a), reflecting that NM integration into AD is entering a growth phase. The position on the S-curve provides insight into strategic technical focuses, guiding further Research and Development (R&D) efforts to optimize and expand the technology.

Following the life cycle framework by Sinisterra et al. [33], a technological system progresses through conception, birth, growth, maturity, and decline, each with distinct goals: "make it work" in the conception stage, "make it work properly" in the birth stage, "maximize performance or efficiency" in the growth stage, "maximize reliability" in the maturity stage, and "minimize cost" in the decline stage [52]. Given the TMR level, NM technology in AD is moving from birth to growth phase, expected to reach maturity around 2037. Kim et al. [53] indicate that technologies with a TMR near 10 % are emerging, which aligns with findings for NM applications in AD, where early-stage research is focused on laboratory-scale studies to understand NM performance under ideal conditions. As technology enters in the growth phase, attention will shift to optimizing production methods and assessing scalability.

The PPA for NM technology in AD was estimated at 82, implying continued growth in intellectual property output. This suggests an upward trend in patent applications as technology transitions to the growth phase, driven by increased R&D activity. The total of 10 patent filings in 2016 may be a precursor to sustained innovation. According to Urbina-Suarez et al. [54], AD represents a mature technology in industrial applications, capable of temporarily mitigating impacts from hard-to-degrade waste contaminants. However, challenges persist, particularly in the disposal of additives, which are often incinerated, regenerated, or replaced. Current research trends thus emphasize the development of stable, naturally derived, regenerable additives, including NMs with large surface areas to enhance AD efficiency.

As indicators, TMR and PPA provide valuable foresight for directing future R&D in NM-based AD technologies. In early life cycle stages, new

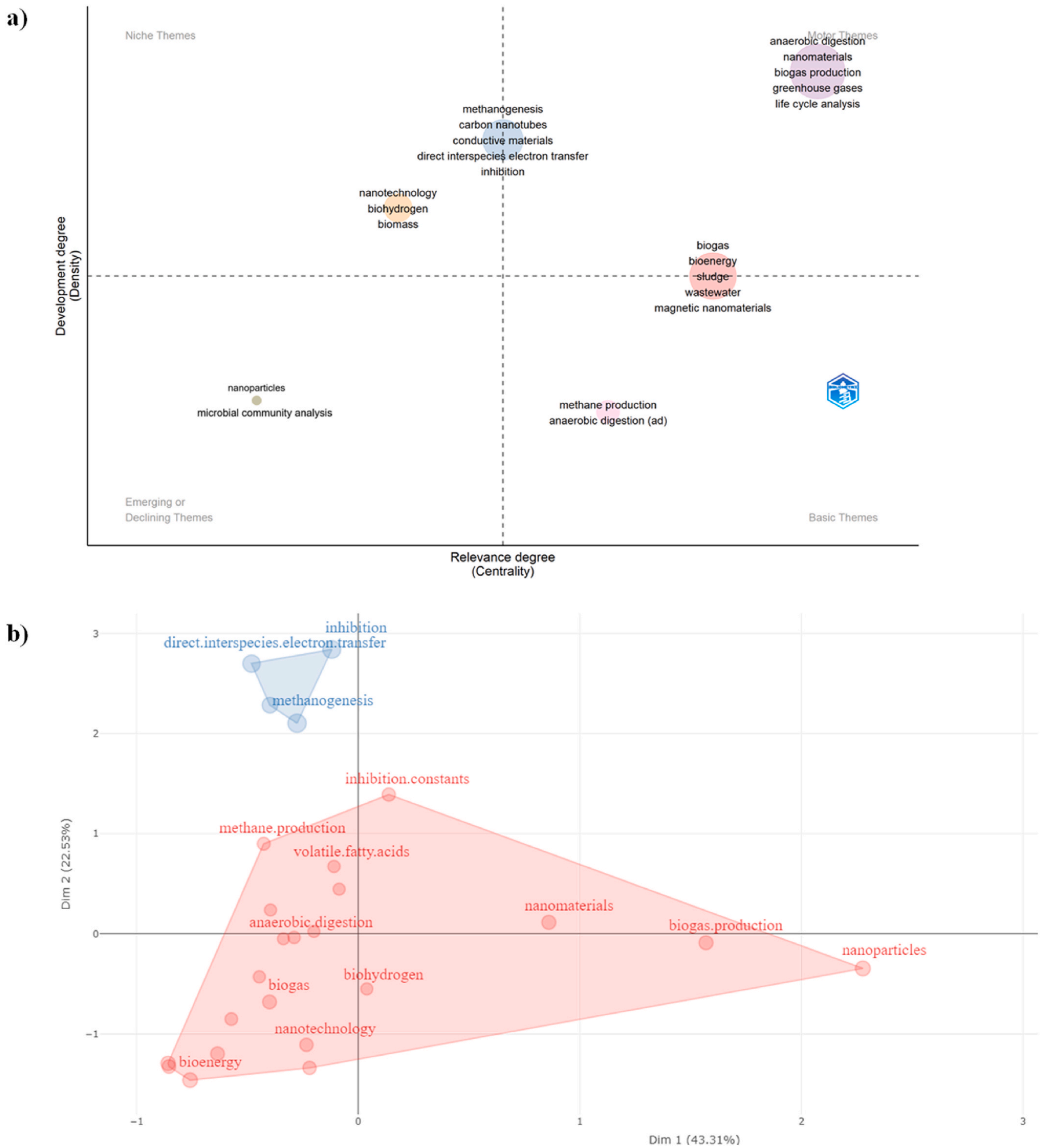

Fig. 3. (a) Thematic map showing trends in the application of NMs in AD; (b) MCA related to the use of nanomaterials in the AD of organic waste.

functionalities and efficiency improvements are prioritized, whereas maturity emphasizes reliability and cost reduction. Based on the current TMR of 10.85 % (Fig. 5), research focused on new functionalities and efficiency optimization for NM applications in AD presents significant invention opportunities.

The ERL of NM technology in AD is estimated at 21 years, projecting that 90 % of patents will be achieved by 2037 (Fig. 5). While the model predicts practical ERL at 13 years, critical issues, including continuous-flow reactor evaluations, NM performance stability, and AD stabilization, need addressing within this timeframe. This aligns with Hollas et al. [55], who used similar models to analyse AD technologies in circular economy applications, such as manure management. As NM technology advances through the growth phase, competition among tech-focused companies is expected to drive innovations centred on reliability and efficiency, leveraging established knowledge. Therefore, ERL and TMR indicators underscore both immediate and extended implications for R&D investment in NM-enhanced AD, supporting renewable energy production and biofertilizer generation from organic waste.

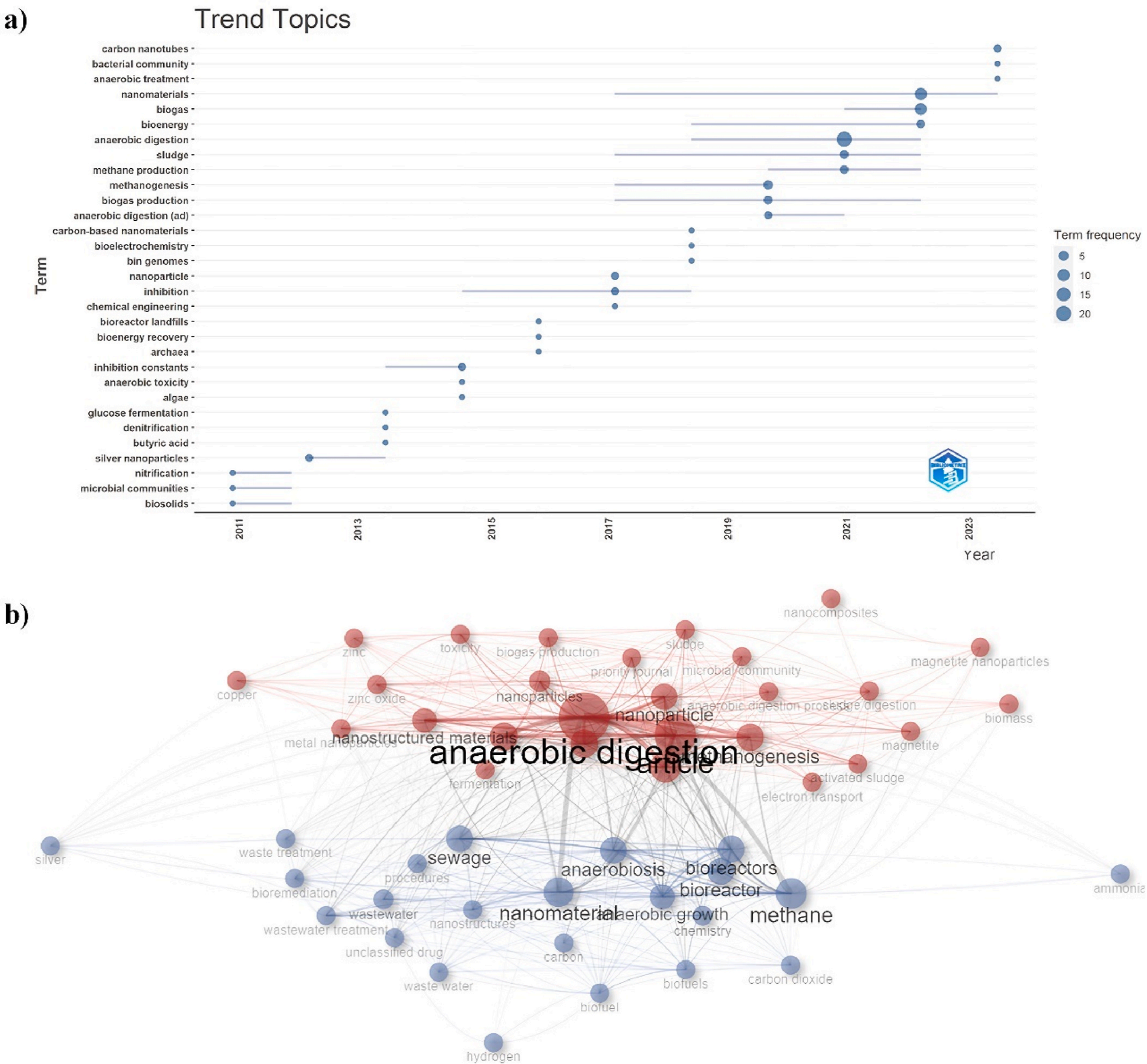

Fig. 4. (a) Evolution of research trends in NM applications in AD of organic waste from 2011 to 2023 (n = 46); (b) Keyword co-occurrence map illustrating thematic relationship in NM and AD research for the period 2011 to 2023.

3.4. Identification of operational and environmental variables affecting NM effectiveness in AD

Fig. 6 presents a dendrogram generated from hierarchical cluster analysis, illustrating keyword connections in the literature on NM applications in AD. These keywords are divided into two primary groups: application tools and process effects, which align with the groupings in Fig. 3b. According to Fig. 6, the analysis identified two main groups, further divided into three subgroups. The blue subgroup pertains to tools used to assess the environmental impacts of NMs in AD, especially with animal manure as a substrate. This focus is consistent with the findings of Dikshit et al. [2] and Kumaret al. [56], who highlighted that NM additives in AD of organic waste enhance the technology's viability as a sustainable energy alternative. Their research suggests that this approach could potentially reduce greenhouse gas emissions by over 80 % in regions where the technology is effectively implemented.

Life cycle assessment (LCA) studies, such as those by Hijazi et al. [51], provide insights into the environmental impacts of different NMs, such as nickel (Ni), cobalt (Co), iron (Fe), and iron oxide (Fe_3O_4), on biogas production. Among these, Co showed the least environmental impact when used to enhance energy production from biogas. However, comprehensive LCAs on NM use in AD remain limited, particularly potential environmental risks posed by NMs in digestates. This necessitates further fundamental research into the effects of NMs in digestates on water or soil ecosystems. Additionally, conducting economic analyses alongside environmental assessments would yield a more comprehensive LCA. As shown in Fig. 6, this subgroup represents the least diverse of the three identified clusters [57].

The green subgroup focuses on the biochemical and physicochemical reactions influenced by NMs within the AD process, particularly regarding inhibition control. Verma et al. [58] emphasize that metal NMs significantly enhance biogas production compared to AD processes

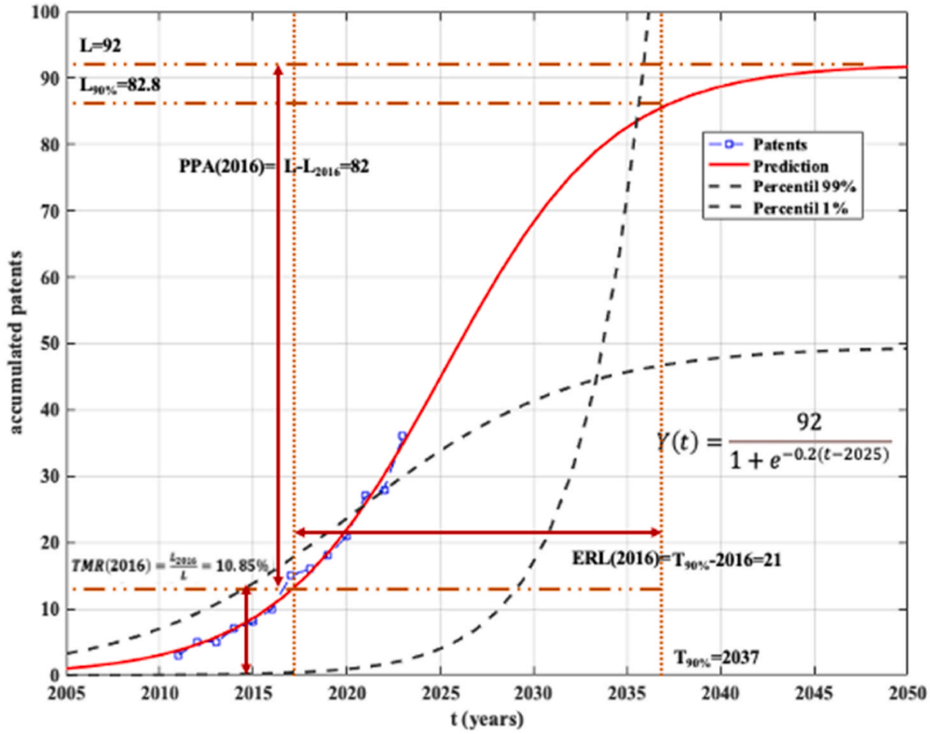

Fig. 5. Technological evolution of NM applications in AD of organic waste, based on the CVT of patents and the logistic growth model fit.

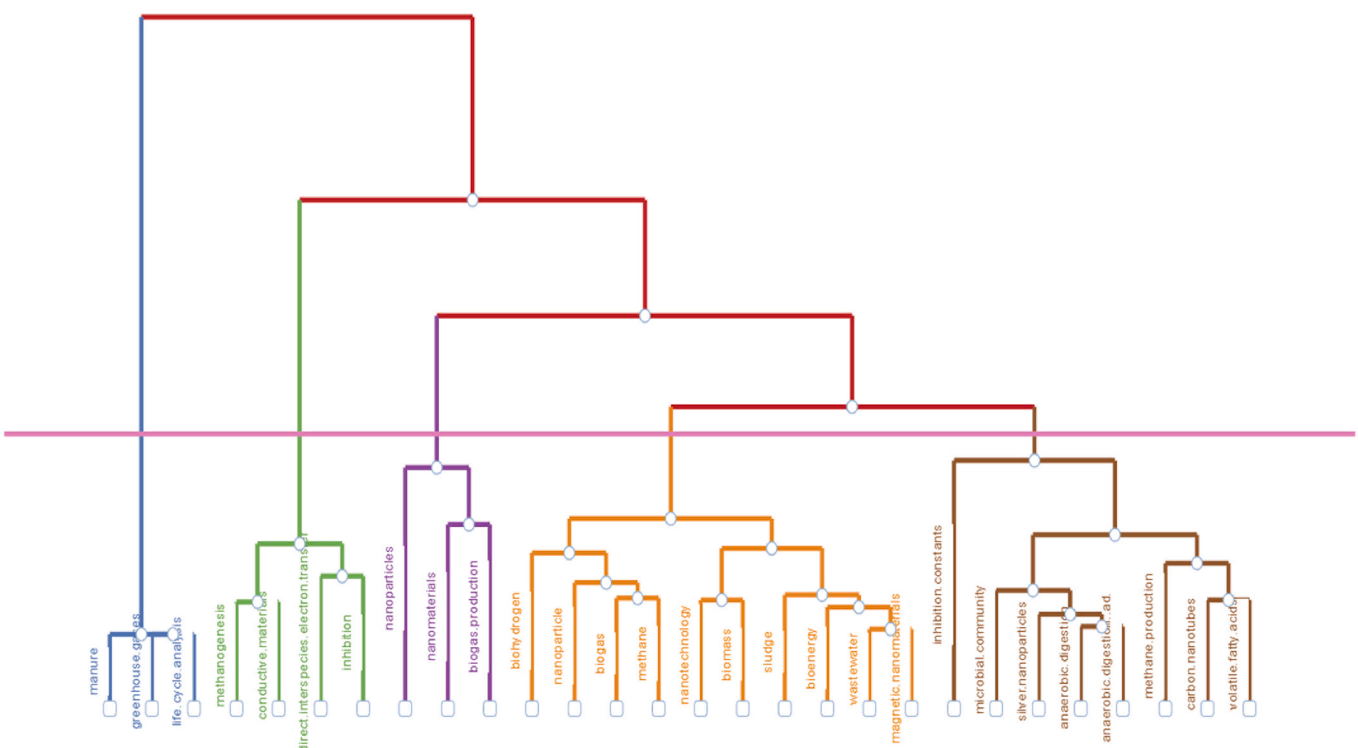

Fig. 6. Dendrogram of hierarchical cluster analysis showing keyword connections in the literature on NM applications in AD.

without these additives. In contrast, Wang et al. [59] found that zeolite NMs could reduce metabolite inhibition (e.g., ammonium) in AD through the Ca^{2+}/NH_4^+ pathway, improving syntrophic oxidation of propionate. Moreover, zeolite NMs mitigate inhibition from other compounds in organic waste, such as phenols and long-chain fatty acids, aiding in the preservation of methanogenic communities. Barrena et al. [29] reported that magnetite NMs significantly reduce VFAs in batch reactors.

The red subgroup, the largest and most diverse, focuses on the effect of NMs on value-added by-products in AD, notably biogas (quality and quantity) and by-products like biohydrogen and short-chain VFAs. This subgroup also includes research on optimizing NM use in the AD of wastewater treatment plant (WWTP) sludge to increase biogas production. WWTP sludge is often used as an AD substrate due to its homogeneity and operational feasibility. This is consistent with the findings from Khan et al. [22], who reported that from 2010 to 2020, NM research in AD, particularly methane production from sludge, grew significantly, making it as a central research area.

Table 1 summarizes the operational and environmental factors examined in NM-enhanced AD of organic waste, including waste type, inoculum source, methane yield, NM type, study scale, NM dosage, and kinetic analysis. WWTP sludge dominates as the most studied waste type, consistent with findings from Fig. 6. For inoculum, sources primarily include anaerobic biomass from domestic or industrial WWTPs and animal manure, particularly pig manure. Hossain et al. [60] note that inoculum type significantly influences the quality and yield of biogas, with mixed inocula increasing biogas production by 2–3 times. Similarly, Silwadi et al. [61] found that combining bovine, camel, and poultry manure positively impacts biogas production, yet research on the effects of NMs on these mixed inocula remains limited, particularly regarding microbial diversity degradation.

Temperature is a critical factor in AD, influencing microbial kinetics, gas-liquid transfer, and biogas quality and quantity. Most studies have been conducted at mesophilic conditions (35–40 °C), with a few at thermophilic conditions (55 °C). However, no research has addressed on NM effects in psychrophilic AD, despite the fact that around 88 % of the global population lives in psychrophilic zones. Research in this area has shown promising energy yields [62]. Jaimes-Estévez et al. [63] and Martí-Herrero et al. [64] demonstrated the potential of psychrophilic AD for organic waste in South America, highlighting a niche for further study on NM applications in cold conditions. This gap represents a significant research opportunity, as Akindolire et al. [65] pointed out, calling for studies on metal NMs (both individually and combined) in psychrophilic AD. Research in this area should document interaction pathways between key AD enzymes and NMs under psychrophilic conditions, focusing on value-added products like methane yield.

Most experiments on NM-enhanced AD have been conducted in batch mode at laboratory scale (BMP assays), underscoring the need to investigate semi-continuous and continuous operations, along with scale-up studies to pilot and full-scale reactors. These studies are essential for developing design criteria and assessing economic viability for real-world applications. Findings from Fig. 5 indicate that NMs in AD are still in early technological development, emphasizing the need for further investigation to refine reactor design and operation. Rossi et al. [66] stressed the importance of reactor configuration and operating conditions on by-products like VFAs, highlighting the potential for insights from pilot-scale studies to support industrial-scale implementation.

The duration of experiments in NM-enhanced AD varies significantly, ranging from 1.25 to 72 days. This extended duration in certain studies is likely due to the nature of BMP assays for high-solid-content wastes, which can span 20–100 days, with a typical range between 28 and 30 days [93,94]. Such variation in processing times may also be attributed to the specific type of NM used, as metallic NMs are known to reduce the degradation lag phase, while carbon-based NMs may extend it [95].

Studies predominantly use metallic NMs, composed of metals like Al, Au, Fe, Pt, Ag, Ti, Cu, Zn, Mg, and Ni, typically within a particle size range of 10–100 nm [96]. These metallic NMs enhance AD performance by stimulating microbial growth and permeating cell membranes, facilitating the breakdown of complex macromolecules into simpler monomers accessible for microbial consumption. However, studies like those by Rocha-Meneses et al. [96] suggest that metallic NMs should be applied at very low concentrations (<10 mg/L) to avoid the generation of inhibitory substances that could compromise process stability and efficiency. In contrast, Devi et al. [97] reported increased biogas yields with NM concentrations between 50 and 70 mg/L, highlighting the need for further studies on dosage optimization based on specific NM types and the economic impact of scaling up, as higher doses may increase operational costs. Carbon-based NMs, including granular and powdered activated carbon, biochar, carbon cloth, single- and multi-walled carbon nanotubes, graphite, and graphene [98], are also used in AD studies. These NMs can be categorized based on dimensionality: zero-dimensional NMs (e.g., graphene quantum dots, carbon quantum dots), one-dimensional NMs (e.g., nanotubes, nanofibers), and two-dimensional NMs (e.g., graphene) [99]. In AD, carbon-based NMs help restructure microbial consortia and enhance methane and biogas production rates.

NM application in the AD has produced a wide range of methane yields (4.03–1200 $mLCH_4\ gVS^{-1}$), organic matter removal efficiencies (37.5 %–97.4 %), VFA concentrations (1–6690 mg/L), and pH values (5.9–8.3). These variations likely result from differences in waste characteristics, NM types, and doses used across studies. NMs are recognized as an emerging additive with potential economic value in AD, enhancing catalytic efficiency and thus improving biogas quality and yield [100]. However, large-scale impacts of NMs remain under debate. As of 2019, no universally applicable guidelines existed for implementing NM-enhanced AD at an industrial scale [17], and this situation remains largely unchanged. According to the predictive model (Fig. 5), such commercial guidelines may only begin to take shape around 2040.

Mathematical models are critical for optimizing AD processes, particularly for maximizing biogas production and evaluating economic feasibility [3]. Most models applied in AD are theoretical, analytical, or statistical, designed to explain process dynamics [101], predict methane yields [102], evaluate inhibition effects, and determine gas-liquid mass transfer [3]. The most common models applied were semi-empirical, such as the modified Gompertz and first-order kinetic models, favoured for their simplicity and limited parameter requirements. However, these models only capture hydrolysis and cannot simulate critical anaerobic process scenarios, such as acidification or pH dynamics, VFA concentrations, and methane content [103]. More advanced models like ADM1 could improve insights into the anaerobic process, simulating complex conditions while reducing experimental requirements, time, cost, and risk [104], particularly important when analysing emerging additives like NMs. Model calibration would be essential, considering NM addition may alter microbial species and metabolic pathways.

Simulating AD process with computational tools, especially AI-based methods, supports large-scale technology implementation. In recent years, AI applications have gained prominence due to their strong predictive capabilities for AD performance and biogas yields [105]. Compared to traditional analytical and statistical models, AI techniques are increasingly recognized for their effectiveness in assessing NM effects in AD, accelerating the path toward industrial-scale adoption.

3.5. Analysis of the effect of NM use on key variables in AD

Fig. 7 shows the effects of NMs on methane production, categorized by waste type in AD. Studies using manure (Fig. 7a) found that iron-based NMs had a greater positive effect on methane production compared to copper-based NMs. Iron not only reduces redox potential, fostering a favourable anaerobic environment, but also enhances key enzyme activities, particularly in the hydrolytic phase [106], which is often the rate-limiting stage for many organic wastes [107]. Hassanpourmoghadam et al. [108] reported that Fe_3O_4 NMs induce beneficial changes in microbial communities, increasing hydrolytic enzyme activity, coenzyme F420 concentrations, and DIET between bacteria and methanogenic archaea. In contrast, copper-based NMs tend to inhibit due to their toxicity to anaerobic microbial consortia, leading to lower biogas quality [109].

For lignocellulosic waste, characterized by its recalcitrant structure due to lignin-cellulose cross-linking, methane production tends to be lower. NMs such as Au, CeO_2, TiO_2, and Fe_3O_4 are more effective with this type of substrate (Fig. 7b), while Ag NMs had the least impact on methane production, likely due to Ag's bactericidal effects that disrupt

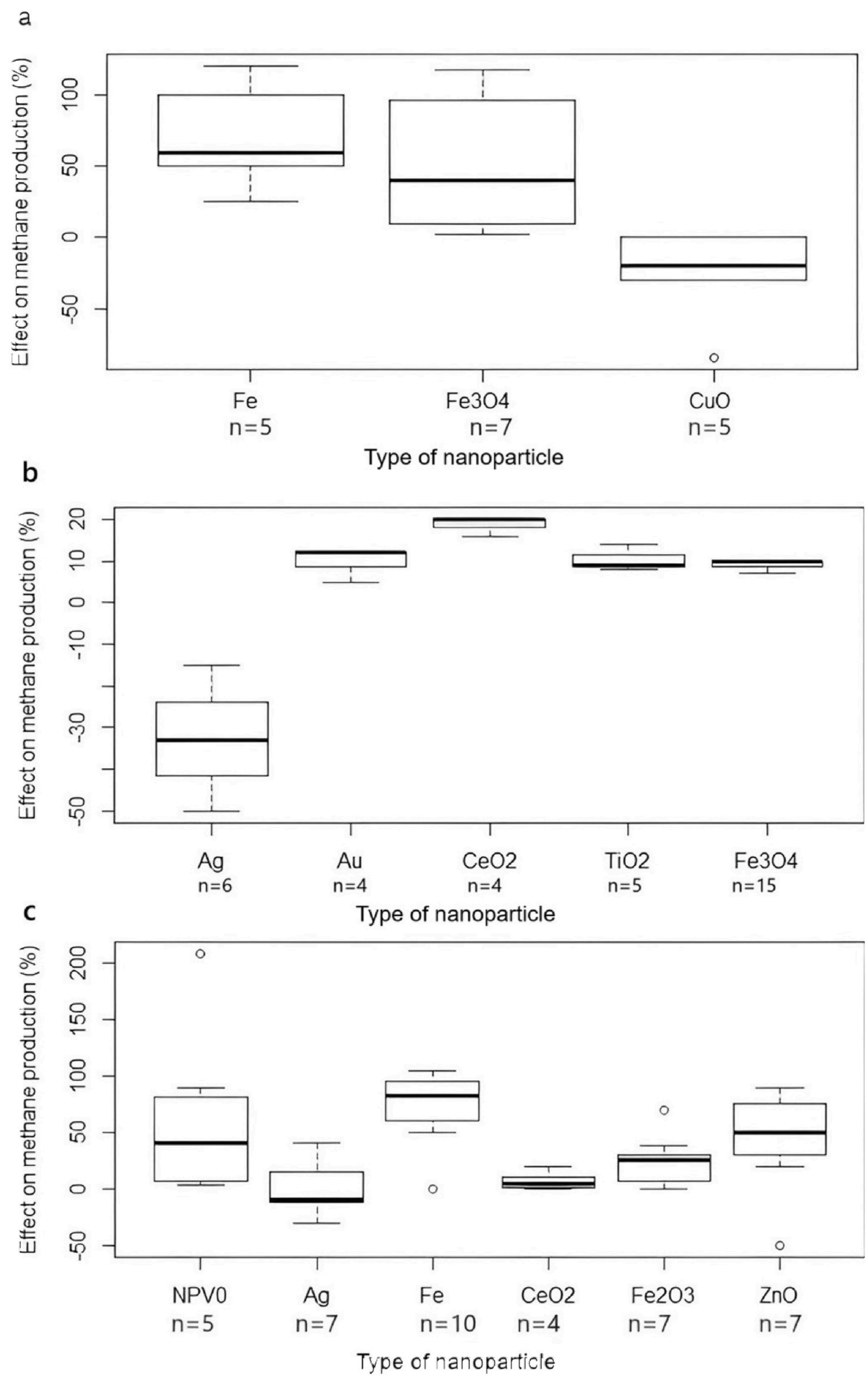

Fig. 7. Effect on methane production by substrate type and metallic NM: (a) NMs used in manure; (b) NM used in lignocellulosic waste; (c) NM used in sludge.

microbial DNA and cell membranes [110]. CeO_2 NMs increased methane yield moderately, attributed to their unique oxygen-releasing capability, which can impact microbial metabolism, though increases in methane production did not exceed 20 % [111].

WWTP sludge was the most commonly studied substrate (Fig. 7c), absorbing contaminants from wastewater treatment that make it challenging for AD. Zero-valent iron (ZVI) showed the most positive effect, boosting methane production by up to 70 % compared to controls, followed by ZnO and Fe_2O_3. In contrast, Ag and CuO NMs had minimal effects, likely due to their inhibitory impacts on microbial and physicochemical processes AD. For example, Ag NMs can release metal ions that bind to and inactivate cellular proteins and nucleic acids in AD [112]. Additionally, CeO_2, despite its effectiveness with lignocellulosic waste, demonstrated less consistent results with sludge, potentially due to its effect on functional microbial groups critical for sludge degradation [113].

Fig. 8 highlights the predominant use of metallic NMs, particularly transition metals, in enhancing methane yields in AD, compared to carbon-based NMs. This analysis associated with methane performance was carried out for batch reactors, since these represented around 90 %

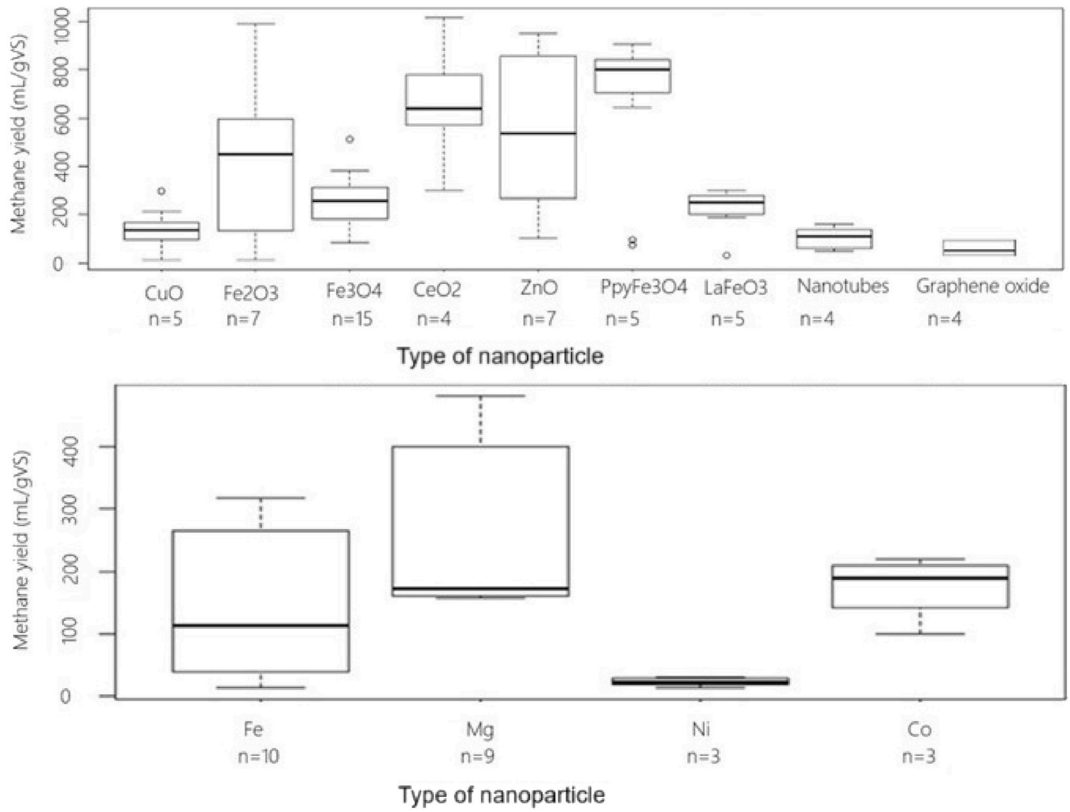

Fig. 8. Methane yield based the type of NM applied in AD of organic waste.

of the articles identified for this variable, thus allowing an analysis of the results at the same feed scale of the reactors in each study. Among metallic NMs, Fe is the most widely used, appearing in 42 samples, including alloys. Its abundance in nature and extensive industrial applications make it more accessible than other metals. Additionally, magnetic metallic NMs, such as Fe-based materials, can be easily separated from the digestate after digestion, adding operational convenience. The state and form of Fe applied in AD offer various benefits. For example, ZVI enhances methane production by releasing hydrogen during corrosion/oxidation, which serves as an electron donor for methanogens, activating the hydrogenotrophic metabolic pathway. It also supports homoacetogenic pathways by facilitating acetic acid production, which acetoclastic methanogens can then convert to methane [30]. This hydrogen release creates a favourable reductive environment for methanogenesis [114]. Other Fe-based NMs, such as Fe_2O_3 and Fe_3O_4, dissolve in water and generate Fe (II) and Fe (III), serving as essential micronutrients for microbial activity or as electron donors in redox reactions that drive the conversion of organic matter to methane [115], thereby contributing to elevated methane yields (see Fig. 8).

In contrast, methane yields associated with the use of Ni-based NMs are the lowest among metallic NMs, likely due to toxicity issues at certain doses. Even low concentrations of Ni (e.g., 1 mg per g-TSS) can be toxic to acetoclastic methanogens, and higher doses can inhibit multiple phases of the AD process [116]. Therefore, understanding the optimal Ni concentration at the nanoscale remains essential, as Ni, in controlled doses, has been reported to stimulate methane production [117]. Further research is necessary to elucidate the mechanisms of Ni in AD and to optimize its application for methane yield enhancement.

The application of carbon-based NMs in AD has garnered significant interest due to their advantageous physical and chemical properties, such as high electrical conductivity and adsorption capacity. These properties support microbial growth by creating adaptable environmental conditions. However, high-cost limits widespread use in AD, which may explain their limited application [26]. Dosage is another critical factor; for instance, Baniamerian et al. [118] indicate that high concentrations of graphene (>2 g L^{-1}) can inhibit microbial activity, suggesting that cytotoxicity could become an adverse effect at elevated doses.

To address these challenges, researchers like Liu et al. [119] have explored the potential of metal-carbon hybrids, known as metallogenic hybrids, to reduce toxicity while leveraging the benefits of both material types. These hybrids, characterized by high porosity, multifunctionality, and customizable structures, hold promise for AD applications. Furthermore, their adaptability and scalability could be enhanced through machine learning techniques. However, further research is needed to evaluate the sustainable application of these hybrids in biological processes.

A synergistic or antagonistic analysis of NM applications revealed that NMs could significantly enhance methane production in AD (Fig. 9a). Methane yield improvements ranged from −10 % to 50 %, indicating variability in NMs' ability to stimulate microbial consortia and initiate organic matter degradation. Ag NMs generally exhibited synergistic effects, increasing methane production by 15 %–20 %, although reductions up to 20 % were also observed. Mg NMs also improved yields, with methane increases of 17 %–30 %, while Fe NMs showed no antagonistic effects, boosting yields by up to 25 %. In contrast, Ni and CuO exhibited inhibitory effects, reducing methane production by up to 7 % and 5 %, respectively. The addition of Fe_2O_3, Fe_3O_4 and CeO_2 improved methane yields by 5 %–63 %, with Fe_3O_4 performing best. ZnO, TiO_2, and NPV0 displayed considerable variability, but overall demonstrated synergistic effects by enhancing biological activity and methane production. NPV0 increased methane yields by up to 55 %, with an average increase of 27 %, followed by TiO_2 at 24 % and ZnO at 15 %. Carbon-based NMs, although generally synergistic, yielded relatively low increases, not exceeding 5 %. Significant effects on methane production were found with Fe_3O_4 ($p = 0.013$), Fe_2O_3 ($p = 0.038$), CeO_2 ($p = 0.042$), ZnO ($p = 0.035$), Ppy/Fe_3O_4 ($p = 0.017$), $LaFeO_3$ ($p = 0.003$), as well as Ni, Mg, Co, Fe ($p = 0.014$),

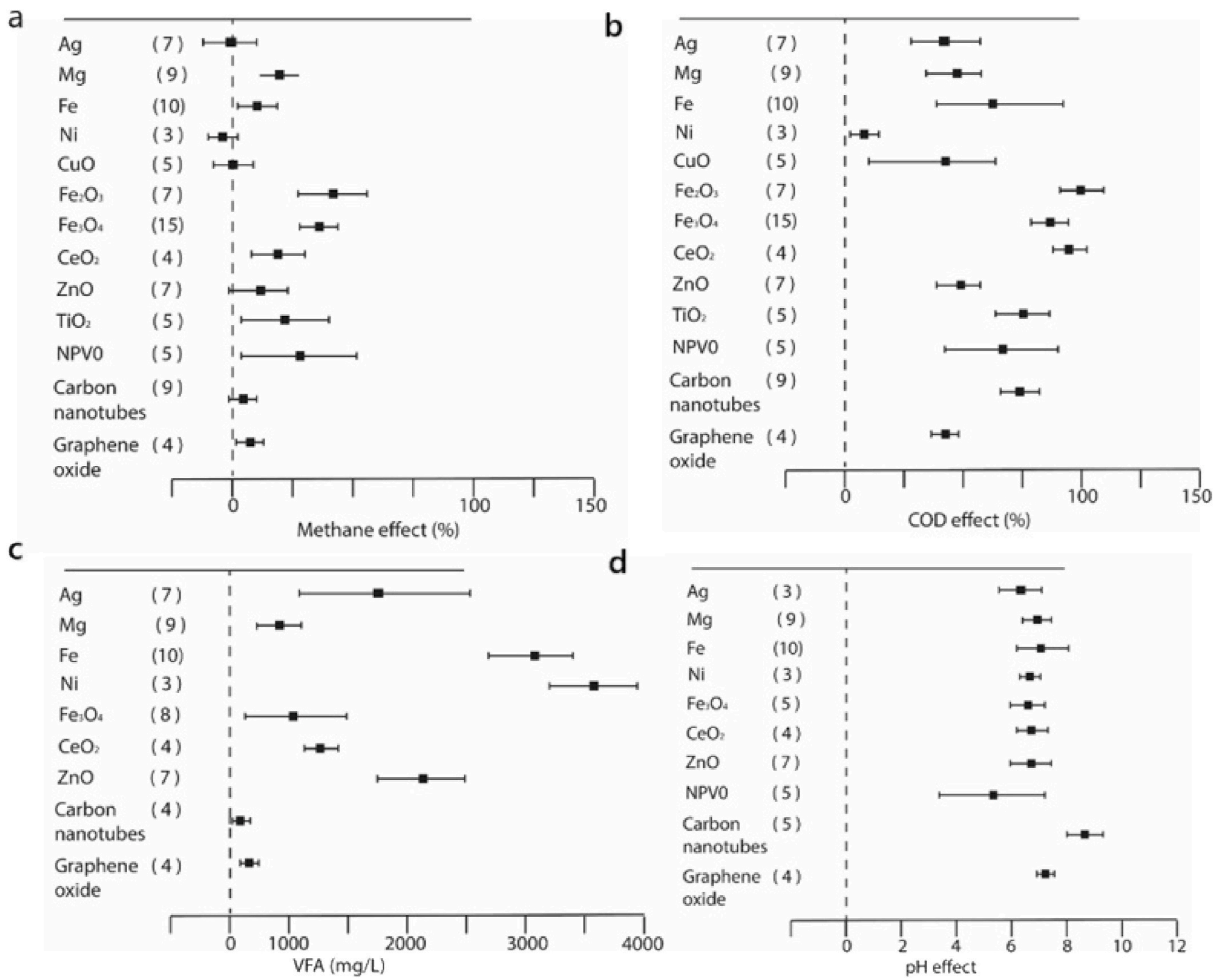

Fig. 9. Effects of NM application on key monitoring variables during AD of organic waste: (a) Methane production; (b) COD reduction; (3) VFA concentration; and (d) pH levels.

implying that these metal-based NMs are valuable for accelerating the AD process and improving byproduct quality. Conversely, no significant effects ($p > 0.05$) were observed with carbon-based NMs or CuO in methane production.

NMs also positively impacted organic matter removal, as indicated by COD reduction (Fig. 9b). Ni NMs achieved limited COD reduction (10 %–15 %), while Ag, Mg, and Fe exhibited COD removal rates of 50 %–60 %, with Mg showing lower variability than Fe, which ranged from 28 % to 90 %. CuO, Fe_2O_3, Fe_3O_4, and CeO_2 achieved the highest COD removal rates (90–98 %), consistent with their potential for high methane yields. ZnO had a reduced COD effect, averaging 52 %, possibly due to toxicity. Carbon-based NMs showed mixed results; nanotubes achieved up to 80 % COD removal, whereas graphene oxide reached only 50 %. This indicates that NMs can enhance contaminant removal in AD, although in some cases, the production of primary metabolites, such as VFAs, may elevate organic matter concentrations in the effluent. Significant COD reduction was observed with Fe ($p = 0.043$), Fe_2O_3 ($p = 0.01$), Fe_3O_4 ($p = 0.01$), CeO_2 ($p = 0.01$), ZnO ($p = 0.037$), TiO_2 ($p = 0.02$), NPV0 ($p = 0.042$), nanotubes ($p = 0.01$), and graphene ($p = 0.016$). In contrast, Ag, Mg, Ni, and CuO show no significant effects ($p > 0.05$) on COD reduction. Although CuO achieved high COD removal, its results were highly variable.

Regarding VFA production (Fig. 9c), Ag NMs increased VFA concentrations to levels above 2500 mg/L, with the likely average around 1800–1900 mg/L, which may explain lower methane yields observed in this review. Fe and Ni NMs led to VFA levels exceeding 3000 mg/L, with Fe averaging 3245 mg/L and Ni 3600 mg/L, although with high variability depending on substrates and operational conditions. Fe_2O_3 produced VFA in the range of 100–1750 mg/L. Carbon-based NMs had the lowest VFA levels, consistently below 700 mg/L, though methane production remained low, suggesting alternative metabolic pathways, potentially producing CO_2 instead. Overall, NMs did not significantly impact pH ($p > 0.05$) (Fig. 9d), which remained between 6.5 and 8, except for nanotube NMs, which reached pH values close to 9. In AD, pH stability depends primarily on carbonic acid and VFAs. Higher VFA levels are neutralized by bicarbonate alkalinity, resulting in volatile acid alkalinity [120]. NMs influence VFA dynamics in AD; for example, Ziganshina and Ziganshin [84] found that Fe_3O_4 and nanotube NMs promotes earlier consumption of acetate and butyrate, hereby increasing methane production. NMs such as Ag ($p = 0.044$), Mg ($p = 0.015$), Fe_2O_3 ($p = 0.034$), CeO_2 ($p = 0.017$), ZnO ($p = 0.048$), nanotubes ($p = 0.001$), and graphene ($p = 0.001$) help reduce VFA concentrations, minimizing inhibitory effects led by these primary metabolites. Ni- and Fe-based NMs, however, had no significant impact on VFA reduction ($p > 0.05$).

Among the NMs studied, transition metals, particularly Fe-based

NMs, demonstrated the most positive impact on AD performance, not only enhancing methane yield but also improving COD removal and VFA reduction. This effect may be attributed to iron's role as a beneficial trace element in AD. Various iron compounds, such as ferric oxide, zero-valent iron, and ferric chloride, are already used to improve AD efficiency [121]. Iron NMs are especially promising due to their strong reducibility and quantum size effects, which enhance reactor performance. These NMs increase yields of value-added byproducts (e.g., methane, hydrogen, organic acids, and others), mitigate VFA and ammonia accumulation, and create a favourable reductive environment through in situ hydrogen release, which supports biogas production efficiency [122].

3.6. Possible mechanisms of NM-enhanced AD

The incorporation of NMs into AD systems has emerged as a promising approach to improve process performance and methane production. Based on their physicochemical nature, NMs used in AD systems can be classified into three main categories [56]: i) conductive zero-valent metals (CZVMs), such as silver (Ag), magnesium (Mg), nickel (Ni), cobalt (Co), and iron (Fe); ii) metal oxide, including titanium dioxide (TiO_2), zinc oxide (ZnO), ferric oxide (Fe_2O_3) and magnetite (Fe_3O_4); and iii) carbon-based conductive NMs, such as carbon nanotubes (CNTs) and graphene oxide (GO). The enhancement effects of NMs on AD performance arise from their ability to influence microbial activity, facilitate electron transfer, and contribute to process stability. The specific mechanisms by which NMs improve methane production depend on their physicochemical interactions with microbial consortia and biochemical pathways [56]. Building upon current advancements, the possible benefits of NMs in AD can be categorized into five major mechanisms: i) Facilitation of electron transfer efficiency; ii) Improvement of hydrolysis and acidogenesis efficiency; iii) Stimulation of methanogenic activity; iv) Mitigation of inhibitory effects and detoxification; and v) Modulation of microbial community structure.

(1) Facilitation of electron transfer efficiency

Electron transfer efficiency is a critical factor in syntrophic microbial interactions, particularly between fermentative bacteria and methanogenic archaea [123]. The diffusion capacities of key metabolites, such as hydrogen and formate, often limit methane production due to mass transfer constraints and equilibrium-related inhibition [124]. NMs have been shown to enhance both DIET and extracellular electron transfer (EET), thus accelerating overall AD performance. Conductive NMs, including CNTs, GO, and Fe_3O_4, act as electron mediators, facilitating rapid interspecies electron exchange between syntrophic bacteria and methanogens [125–128]. This process bypasses the slower hydrogen- and formate-mediated electron transfer pathways, leading to a more efficient methane production process. Additionally, metal-based NMs (e.g., Fe_3O_4, manganese oxides, and TiO_2) can interact with microbial electron transport chains, enhancing energy flow and boosting microbial metabolic activities [129]. Moreover, transition metal nanoparticles (e.g., Ni-, Co-, and Fe-based NMs) can serve as electron sinks, providing additional electron donors for methanogenesis [130]. Ni, in particular, is a crucial component of enzymes such as F_{430}, which plays a role in methanogenic archaea [131]. The presence of these nanoparticles can optimize energy capture from organic matter and improve the overall metabolic efficiency of microbial communities.

(2) Enhanced hydrolysis and acidogenesis

As the rate-limiting step in AD, hydrolysis determines the efficiency of complex organic matter degradation into fermentable intermediates. NMs can accelerate hydrolysis through multiple pathways. Certain NMs, such as Fe_3O_4, and chitosan-based nanoparticles, can serve as enzyme carriers, protecting hydrolytic enzymes from degradation and enhancing their catalytic efficiency [132]. Immobilization on NM surfaces prevents enzyme autolysis and denaturation while improving enzyme rigidity. Magnetic Fe_3O_4 nanoparticles also enable enzyme recovery and reuse, enhancing long-term process efficiency. Beyond enzyme stabilization, metal oxide nanoparticles (e.g., TiO_2, Fe_3O_4, and ZnO) improve hydrolysis by disrupting biomass structure, exposing more surface area for microbial attack [133]. These nanoparticles interact with biomass surfaces, destabilizing cell walls and accelerating substrate decomposition [134]. During acidogenesis, NMs can influence acidogenic microbial populations and enhance the conversion of hydrolyzed intermediates into VFAs. Certain metal oxides (e.g., Fe_3O_4 and ZnO) can promote acidogenic bacterial growth by releasing trace elements essential for enzymatic activity [135]. Additionally, alkaline NMs (e.g., CaO, MgO) buffer pH fluctuations by neutralizing excessive VFAs, preventing acid accumulation that could inhibit acidogenic bacteria.

(3) Stimulation of methanogenesis

Methanogenic archaea require specific trace metals and electron donors to facilitate methane production. NMs enhance methanogenesis through multiple pathways. Trace metals such as Ni, Co, Mo, and Fe, serve as cofactors for key methanogenic enzymes, including methyl-coenzyme M reductase (MCR) and formate dehydrogenase, thereby increasing enzymatic activity and methane production rates [20,136,137]. Additionally, graphene-based materials and biochar facilitate stable biofilm formation and improve methanogen retention by providing high surface area and electrical conductivity, which support microbial colonization [138,139]. Furthermore, NMs can shift metabolic pathways in favor of hydrogenotrophic and acetoclastic methanogenesis by facilitating DIET [140].

(4) Inhibition mitigation and detoxification

AD performance is often hindered by inhibitory compounds, such as ammonia, heavy metals, and H_2S. NMs mitigate these inhibitory effects through various mechanisms. s ZnO, TiO_2, Fe_3O_4, and biochar-based NMs effectively adsorb inhibitory substances, reducing their bioavailability [141]. Additionally, MgO and CaO-based nanoparticles precipitate ammonium and H_2S as non-toxic salts, thus preventing inhibition of methanogenesis [142]. Some NMs, particularly Fe_3O_4 and chitosan-functionalized nanoparticles, chelate heavy metals, thereby reducing their toxicity toward microbial populations [143]. Chitosan-Fe_3O_4 composites have been shown to effectively remove heavy metals like cadmium (Cd^{2+}) from aqueous solutions through adsorption mechanisms [143].

(5) Structural and functional microbial community shifts

The introduction of NMs can alter microbial community composition, favoring microbial populations that enhance AD performance. Conductive NMs facilitate DIET, enriching electron-transferring microorganisms such as *Geobacter* and *Methanosaeta*, which are proficient in electron transfer and methanogenesis [144]. Additionally, certain NMs can selectively inhibit sulfate-reducing bacteria (SRB), reducing competition for substrates with methanogens. For example, magnesium hydroxide nanoparticles have demonstrated antibacterial activity against SRB, thereby mitigating their inhibitory effects on methanogenesis [145].

These mechanisms may act synergistically or independently, depending on the type and concentration of NMs incorporated into the AD system. The enhancement effects of NMs are highly dependent on their physicochemical properties, as well as the operating conditions of the AD process. While NM-enhanced AD has shown promise in lab-scale studies, further research is needed to assess long-term stability, economic feasibility, and environmental implications for full-scale applications. Future studies should focus on optimizing NM selection and dosage for diverse substrates and reactor configurations.

3.7. Opportunities and challenges in NM applications in AD

This section discusses seven critical opportunities and challenges for advancing NM applications in AD of organic waste.

(1) Exploring NM effects on microbial communities in batch and continuous operations

While research has primarily focused on NM characteristics and methane yield, recent studies increasingly examine NMs' effects on microbial communities, including their abundance, diversity, and metabolic functions related to methane production [146]. Most studies have centred on iron- and silver-based NMs, with limited research on titanium, copper, and carbon-based NMs, generally conducted at laboratory scale using substrates like manure or lignocellulosic waste [147, 148]. Further studies should investigate the influence of these less-studied NMs on microbial community dynamics, metabolic functions, and DIET mechanisms. Additionally, research on NM addition strategies, such as single or multiple additions in continuous reactors, could facilitate microbial acclimation, providing insights into syntrophic relationships within microbial communities.

(2) Understanding the impact of NMs on process biochemistry

A deeper understanding of how NMs influence fermentation intermediates, particularly VFAs, is essential. This includes examining the types, quality, and quantity of acids produced and assessing NM effects on biohydrogen electron transfer, which could impact hydrogen yields and overall methane production [149].

(3) Examining the effect of NMs on digestate physicochemical properties

Research has predominantly focused on biogas yield improvements, with limited attention to digestate properties. Iron-based NMs, identified as beneficial for methane production, do not seem to induce chemical toxicity in digestate; however, particle size may impact other properties, which remain unexplored. Further investigation should assess how NMs affect digestate quality, including nutrient release capacity and agronomic potential, when applied to soils. Additionally, the potential for biochar production from digestate containing NM traces could align with biorefinery concepts, enhancing methane production or yielding valuable products like antioxidants and bioplastics [150]. Other applications, such as biopesticide production via solid-state fermentation, represent promising technological extensions for valorising digestate by-products [151].

(4) Evaluating NM application in psychrophilic AD conditions

Most AD studies with NMs have been conducted under mesophilic (35–37 °C) or thermophilic (50–55 °C) conditions, as these temperatures generally yield higher methane production [30]. However, in colder regions where temperatures fall below 18–20 °C, energy efficiency can suffer due to additional heating requirements, which reduces process sustainability [62]. Studies assessing NM effects in AD under psychrophilic conditions are crucial for lowering heating-related energy consumption and operational costs, especially in developing regions where digesters are often operated at lower temperatures. Such advancements could significantly improve organic waste management in colder climates, reducing the carbon footprint through optimized, low-energy alternatives.

(5) Addressing operational and scale-up conditions in AD with NMs

Further investigation is needed on the operational conditions of AD (e.g., batch vs. continuous) and the scalability of NM applications, particularly to overcome mass transfer limitations within the reactor, which are prominent in dry AD where NM dynamics may be affected. Comparative studies evaluating methane production, microbial activity, and methanogenic functions under different operational conditions will provide essential data for technical-economic analysis at a commercial scale, facilitating implementation.

(6) Using optimization tools for process enhancement

Current modelling efforts in NM-enhanced AD rely mainly on semi-empirical models like the first order and Gompertz models (used in 7 studies). However, there is a need for more advanced models to capture NM effects across all AD stages. Machine learning tools, such as artificial neural networks (ANN), random forests (RF), and support vector machines (SVM), could provide predictive insights, optimize parameters, and reduce operational costs. ANNs, for example, have effectively understood AD's complex physicochemical and biochemical interactions, reducing experimental needs and computational demands. Integrating metaheuristic optimization methods (e.g., ant colony optimization, particle swarm optimization) could address the limitations of local optima and improve overall process efficiency, guiding the design of innovative configurations for waste valorisation [152].

(7) Assessing the sustainability of NM use in AD

LCA studies and detailed economic analyses are crucial for understanding the long-term impacts and sustainability of NMs in AD, especially since many NMs originate from non-renewable resources. To the authors' knowledge, no existing studies on LCA for NM-enhanced AD highlight a significant research gap. Such assessments are essential for evaluating environmental sustainability and ensuring viability at the commercial scale.

4. Conclusions

This review concludes the following key points regarding NM applications in AD of organic waste.

- The use of NMs in AD presents a promising approach for enhancing the process stability and biogas production. Studies are primarily concentrated in developed countries, with patent analysis indicating that the technology is still emerging, transitioning from the birth to growth stages, with maturity anticipated by 2037.
- Metadata analysis revealed that NM applications in AD can improve biogas production by up to 25 % compared to conventional AD processes. Iron-based NMs demonstrated the highest performance for methane production in AD of manure, WWTP sludge, and lignocellulosic waste, particularly when combined with other NMs such as Au, CeO_2, and TiO_2. Carbon-based NMs, while effective, tend to produce less biogas and may face industrial limitations due to their high cost.
- Seven main challenges and opportunities were identified for advancing NM research in AD of organic waste: (i) investigating the effects of various NMs on microbial communities to better understand syntrophic relationships and their role in organic matter degradation; (ii) examining NM effects on fermentation intermediates, electron transfer processes, and biogas production; (iii) evaluating the impact of NMs on digestate characteristics, quality, potential agronomic applications, and their role in generating additional bioproducts; (iv) analysing NM application in psychrophilic AD conditions to explore technical and economic feasibility for low-temperature applications; (v) addressing scale-up challenges for AD processes using NMs, focusing on overcoming mass transfer limitations in reactors; (vi) employing optimization tools such as neural

networks, random forests, and support vector machines to generate predictive insights that can enhance AD performance and guide technological design, configuration, and operational parameters (e.g., batch vs. continuous); (vii) conducting LCA and economic analyses to evaluate the sustainability of NM use in AD and its associated by-products.

CRediT authorship contribution statement

Brayan Alexis Parra-Orobio: Writing – original draft, Visualization, Methodology, Investigation, Data curation. **Jonathan Soto-Paz:** Writing – original draft, Visualization. **Silvia Juliana Lara-Franco:** Writing – original draft, Visualization. **María Fernanda Castañeda-Restrepo:** Writing – original draft, Visualization. **Edgar Ricardo Oviedo-Ocaña:** Writing – review & editing, Visualization, Supervision, Methodology, Conceptualization. **Zhongzhong Wang:** Writing – review & editing. **Antoni Sánchez:** Writing – review & editing, Methodology, Conceptualization.

Competing interests

The authors have no relevant financial or non-financial interests to disclose.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.biombioe.2025.108268.

Data availability

Data will be made available on request.

References

[1] M. Khalil, M.A. Berawi, R. Heryanto, A. Rizalie, Waste to energy technology: the potential of sustainable biogas production from animal waste in Indonesia, Renew. Sustain. Energy Rev. 105 (2019) 323–331, https://doi.org/10.1016/j.rser.2019.02.011.
[2] P.K. Dikshit, S.K. Padhi, L. Pattanaik, A. Khan, A. Ranjan, S. Sadhu, A critical review on nanotechnological advancement in biogas production from organic waste, Biomass Conversion and Biorefinery (2023), https://doi.org/10.1007/s13399-023-04432-1.
[3] B.A. Parra-Orobio, J. Soto-Paz, E.R. Oviedo-Ocaña, S.A. Vali, A. Sánchez, Advances, trends and challenges in the use of biochar as an improvement strategy in the anaerobic digestion of organic waste: a systematic analysis, Bioengineered 14 (2023) 2252191. https://www.tandfonline.com/doi/abs/10.1080/21655979.2023.2252191.
[4] S.A. Mohd Johari, M. Ayoub, A. Inayat, S. Ullah, M. Uroos, S.R. Naqvi, S. Farukkh, Utilization of dairy scum waste as a feedstock for biodiesel production via different heating sources for catalytic transesterification, ChemBioEng Rev. 9 (2022) 605–632, https://doi.org/10.1002/cben.202200003.
[5] C.M. Ajay, S. Mohan, P. Dinesh, M.A. Rosen, Review of impact of nanoparticle additives on anaerobic digestion and methane generation, Fuel 277 (2022) 118234, https://doi.org/10.1016/j.fuel.2020.118234.
[6] A.M. Omer, An overview of biomass and biogas for energy generation: recent development and perspectives, Cellul. Chem. Technol. 46 (2012) 477–492, https://doi.org/10.31248/JBBD2016.010.
[7] F. Piadeh, I. Offie, K. Behzadian, J.P. Rizzuto, A. Bywater, J.R. Córdoba-Pachón, M. Walker, A critical review for the impact of anaerobic digestion on the sustainable development goals, J. Environ. Manag. 349 (2024) 119458, https://doi.org/10.1016/j.jenvman.2023.119458.
[8] Y. Duan, Z. Wang, P. Ganeshan, T. Sar, S. Xu, K. Rajendran, R. Sindhu, P. Binod, A. Pandey, Z. Zhang, M.J. Taherzadeh, M.K. Awasthi, Anaerobic digestion in global bio-energy production for sustainable bioeconomy: potential and research challenges, Renew. Sustain. Energy Rev. 208 (2025) 114985, https://doi.org/10.1016/j.rser.2024.114985.
[9] X. Kong, J. Niu, W. Zhang, J. Liu, J. Yuan, H. Li, X. Yue, Mini art review for zero valent iron application in anaerobic digestion and technical bottlenecks, Sci. Total Environ. 791 (2021) 148415, https://doi.org/10.1016/j.scitotenv.2021.148415.
[10] Z.W. He, Z.S. Zou, Y.-X. Ren, C.C. Tang, A.J. Zhou, W. Liu, L. Wang, Z. Li, A. Wang, Roles of zero-valent iron in anaerobic digestion: mechanisms, advances and perspectives, Sci. Total Environ. 852 (2022) 158420, https://doi.org/10.1016/j.scitotenv.2022.158420.
[11] C.D. Dubé, S.R. Guiot, Direct interspecies electron transfer in anaerobic digestion, A review, Biogas Science and Technology (2015) 101–115, https://doi.org/10.1007/978-3-319-21993-6_4.
[12] M. Samer Abdelsalam, Y.A. Attia, M.A. Abdel-Hadi, H.E. Hassan, Y. Badr, Comparison of nanoparticles effects on biogas and methane production from anaerobic digestion of cattle dung slurry, Renew. Energy 87 (2016) 592–598, https://doi.org/10.1016/j.renene.2015.10.053.
[13] S. Vickram, S. Manikandan, S.R. Deena, J. Mundike, R. Subbaiya, N. Karmegam, S. Jones, K. Kumar Yadav, S. woong Chang, B. Ravindran, M. Kumar Awasthi, Advanced biofuel production, policy and technological implementation of nano-additives for sustainable environmental management – a critical review, Bioresour. Technol. 387 (2023) 129660, https://doi.org/10.1016/j.biortech.2023.129660.
[14] M. Daneshvar, M.R. Hosseini, From the iron boring scraps to superparamagnetic nanoparticles through an aerobic biological route, J. Hazard Mater. 357 (2018) 393–400, https://doi.org/10.1016/j.jhazmat.2018.06.024.
[15] C. Parisi, M. Vigani, E. Rodríguez-Cerezo, Agricultural Nanotechnologies: what are the current possibilities? Nano Today 10 (2015) 124–127, https://doi.org/10.1016/j.nantod.2014.09.009.
[16] P. Jadhav, M. Nasrullah, A.W. Zularisam, P. Bhuyar, S. Krishnan, P. Mishra, Direct interspecies electron transfer performance through nanoparticles (NPs) for biogas production in the anaerobic digestion process, Int. J. Environ. Sci. Technol. 19 (2022) 10427–10439, https://doi.org/10.1007/s13762-021-03664-w.
[17] 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. Manag. 251 (2019) 109597, https://doi.org/10.1016/j.jenvman.2019.109597.
[18] E. Casals, R. Barrena, E. Gonzalez, X. Font, A. Sánchez, V. Puntes, Historical perspective of the addition of magnetic nanoparticles into anaerobic digesters (2014-2021), Frontiers in Chemical Engineering 3 (2021) 745610, https://doi.org/10.3389/fceng.2021.745610.
[19] T.A.M. Abdelwahab, A.E.M. Fodah, Utilization of nanoparticles for biogas production focusing on process stability and effluent quality, SN Appl. Sci. 4 (2022) 332, https://doi.org/10.1007/s42452-022-05222-6.
[20] Y.Y. Choong, I. Norli, A.Z. Abdullah, M.F. Yhaya, Impacts of trace element supplementation on the performance of anaerobic digestion process: a critical review, Bioresour. Technol. 209 (2016) 369–379, https://doi.org/10.1016/j.biortech.2016.03.028.
[21] T. Tian, S. Qiao, X. Li, M. Zhang, J. 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.
[22] 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), https://doi.org/10.3389/fbioe.2022.868454.
[23] B. Salehi, L. Wang, Critical review on nanomaterials for enhancing bioconversion and bioremediation of agricultural wastes and wastewater, Energies 15 (2022) 5387, https://doi.org/10.3390/en15155387.
[24] J. Li, C. Li, L. Zhao, X. Pan, G. Cai, G. Zhu, The application status, development and future trend of nano-iron materials in anaerobic digestion system, Chemosphere 269 (2021) 129389, https://doi.org/10.1016/j.chemosphere.2020.129389.
[25] S. Ugwu, C.C. Enweremadu, Enhancing anaerobic digestion of okra waste with the addition of iron nanocomposite (Ppy/Fe_3O_4), Biofuels 11 (2020) 503–512, https://doi.org/10.1080/17597269.2019.1702796.
[26] R.B. Jeyakumar, G.S. Vincent, Recent advances and perspectives of nanotechnology in anaerobic digestion: a new paradigm towards sludge biodegradability, Sustainability 14 (2022) 7191, https://doi.org/10.3390/su14127191.
[27] A. Hassanein, A. Naresh Kumar, S. Lansing, Impact of electro-conductive nanoparticles additives on anaerobic digestion performance - a review, Bioresour. Technol. 342 (2021) 126023, https://doi.org/10.1016/j.biortech.2021.126023.
[28] X. Zhu, E. Blanco, M. Bhatti, A. Borrion, Impact of metallic nanoparticles on anaerobic digestion: a systematic review, Sci. Total Environ. 757 (2021) 143747, https://doi.org/10.1016/j.scitotenv.2020.143747.

[29] R. Barrena, M. del C. Vargas-García, P. Catacora-Padilla, T. Gea, A. Abo Markeb, J. Moral-Vico, A. Sánchez, X. Font, T.J. Aspray, Magnetite-based nanoparticles and nanocomposites for recovery of overloaded anaerobic digesters, Bioresour. Technol. 372 (2023) 128632, https://doi.org/10.1016/j.biortech.2023.128632.
[30] M. Cerrillo, L. Burgos, B. Ruiz, R. Barrena, J. Moral-Vico, X. Font, A. Sánchez, A. Bonmatí, In-situ methane enrichment in continuous anaerobic digestion of pig slurry by zero-valent iron nanoparticles addition under mesophilic and thermophilic conditions, Renew. Energy 180 (2021) 372–382, https://doi.org/10.1016/j.renene.2021.08.072.
[31] R. González, D.C. Peña, X. Gómez, Anaerobic co-digestion of wastes: reviewing current status and approaches for enhancing biogas production, Appl. Sci. 12 (2022) 8884, https://doi.org/10.3390/app12178884.
[32] A.A. Chadegani, H. Salehi, M.M. Yunus, H. Farhadi, M. Fooladi, M. Farhadi, N. A. Ebrahim, A comparison between two main academic literature collections: web of science and scopus databases, Asian Soc. Sci. 9 (2013) 18–26, https://doi.org/10.5539/ass.v9n5p18.
[33] S. Sinisterra, R. Camargo-Amado, D. Triviño, F. Machuca-Martínez, Methodology to prepare patent analysis and the technological maturity cycle, Rev. Fac. Ing. 32 (2023) e14299, https://doi.org/10.19053/01211129.v32.n63.2023.14299.
[34] M.M. Cely-Bautista, G. Castellar-Ortega, J. Jaramillo-Colpas, I.R. Mejía, Trends in the development of metallic and bimetallic nanoparticles: a patents landscape analysis, Ingeniería y Competitividad 25 (2023) 1–12, https://doi.org/10.25100/iyc.v25i3.12798.
[35] J. Soto-Paz, E.R. Oviedo-Ocaña, P. Torres-Lozada, L.F. Marmolejo-Rebellón, P. Manyoma-Velásquez, Composting of biowaste: research trends and relevance in developing countries, Dyna 84 (2017) 334–342, https://doi.org/10.15446/dyna.v84n202.61549.
[36] M. Casallas-Ojeda, L.E. Torres-Guevara, D.M. Caicedo-Concha, M.F. Gómez, Opportunities for waste to energy in the milk production industry: perspectives for the circular economy, Sustainability 13 (2021) 12892, https://doi.org/10.3390/su132212892.
[37] J. Soto-Paz, O. Arroyo, L.E. Torres-Guevara, B.A. Parra-Orobio, M. Casallas-Ojeda, The circular economy in the construction and demolition waste management: a comparative analysis in emerging and developed countries, J. Build. Eng. 78 (2023) 107724, https://doi.org/10.1016/j.jobe.2023.107724.
[38] W. Cui, Y. Wei, N. Ji, Global trends of waste-to-energy (WtE) technologies in carbon neutral perspective: bibliometric analysis, Ecotoxicol. Environ. Saf. 270 (2024) 115913, https://doi.org/10.1016/j.ecoenv.2023.115913.
[39] S. Patiño, Y. Hernández, C. Plata, I. Domínguez, M. Daza, R. Oviedo-Ocaña, W. Buytaert, B. Ochoa-Tocachi, Influence of land use on hydro-physical soil properties of Andean páramos and its effect on streamflow buffering, Catena 202 (2021) 105227, https://doi.org/10.1016/j.catena.2021.105227.
[40] J. Yoon, B. Jeong, W.H. Lee, J. Kim, Tracing the evolving trends in electronic skin (e-skin) technology using growth curve and technology position-based patent bibliometrics, IEEE 6 (2018) 26530–26542, https://doi.org/10.1109/ACCESS.2018.2834160.
[41] L. Gao, A.L. Porter, J. Wang, S. Fang, X. Zhang, T. Ma, W. Wang, L. Huang, Technology life cycle analysis method based on patent documents, Technol. Forecast. Soc. Change 80 (2013) 398–407, https://doi.org/10.1016/j.techfore.2012.10.003.
[42] M. Baumann, T. Domnik, M. Haase, C. Wulf, P. Emmerich, C. Rösch, P. Zapp, T. Naegler, M. Weil, Comparative patent analysis for the identification of global research trends for the case of battery storage, hydrogen and bioenergy, Technol. Forecast. Soc. Change 165 (2021) 120505, https://doi.org/10.1016/j.techfore.2020.120505.
[43] A. Nigussie, B. Dume, M. Ahmed, M. Mamuye, G. Ambaw, G. Berhiun, A. Biresaw, A. Aticho, Effect of microbial inoculation on nutrient turnover and lignocellulose degradation during composting: a meta-analysis, Waste Manag. 125 (2021) 220–234, https://doi.org/10.1016/j.wasman.2021.02.043.
[44] S. Alberici, W. Grimme, G. Toop, Biomethane Production Potentials in the EU. Feasibility of REPowerEU 2030 Targets, Production Potentials in the Member States and Outlook to 2050, 2022. Guidehouse, Editor. Utrecht.
[45] SIE, Egypt ranks 22nd in nanotechnology research. https://www.sis.gov.eg/Story/15090?lang=es, 2018. Accessed December 2023.
[46] M. Elsayed, R. Hassany, M. Soliman, Anaerobic co-digestion of sludge, sugarcane leaves, and *Corchorus* stalks in Egypt, Biomass Conversion and Biorefinery 13 (2023) 2177–2191, https://doi.org/10.1007/s13399-021-01577-9.
[47] L.C. Ampese, W.G. Sganzerla, H.D.D. Ziero, A. Mudhoo, G. Martins, T. Forster-Carneiro, Research progress, trends, and updates on anaerobic digestion technology: a bibliometric analysis, J. Clean. Prod. 331 (2022) 130004, https://doi.org/10.1016/j.jclepro.2021.130004.
[48] J.R. López-Robles, J. Guallar, J. Otegi-Olaso, N.K. Gamboa-Rosales, El profesional de la información (EPI): bibliometric and thematic analysis (2006-2017), Profesional de la información 28 (2019) 1–23, https://doi.org/10.3145/epi.2019.jul.17.
[49] T.I. Assis, R.F. Gonçalves, Valorization of food waste by anaerobic digestion: a bibliometric and systematic review focusing on optimization, J. Environ. Manag. 320 (2022) 115763, https://doi.org/10.1016/j.jenvman.2022.115763.
[50] L. Feng, Z. Gao, T. Hu, S. He, Y. Liu, J. Jiang, Q. Zhao, L. Wei, A review of application of combined biochar and iron-based materials in anaerobic digestion for enhancing biogas productivity: mechanisms, approaches and performance, Environ. Res. 234 (2023) 116589, https://doi.org/10.1016/j.envres.2023.116589.
[51] O. Hijazi, E. Abdelsalam, M. Samer, Y. Attia, B. Amer, M. Amer, M. Badr, H. Bernhardt, Life cycle assessment of the use of nanomaterials in biogas production from anaerobic digestion of manure, Renew. Energy 148 (2020) 417–424, https://doi.org/10.1016/j.renene.2019.10.048.
[52] D. Mann, Hands-On Systematic Innovation, 2007.
[53] J. Kim, Z. Kim, D.H. Lee, Prediction of the emergence of solid-state battery technology in the post-lithium ion battery era: a patent-based approach, Int. J. Green Energy 21 (2024) 1210–1225, https://doi.org/10.1080/15435075.2023.2244060.
[54] N.A. Urbina-Suarez, A.C. Angel-Ospina, G.L. Lopez-Barrera, A.F. Barajas-Solano, F. Machuca-Martínez, S-curve and landscape maps for the analysis of trends on industrial textile wastewater treatment, Environ. Adv. 15 (2024) 100491, https://doi.org/10.1016/j.envadv.2024.100491.
[55] C.E. Hollas, H.C. Rodrigues, V.M.A. Oyadomari, A.C. Bolsan, B. Venturin, G. Bonassa, D.C. Tápparo, H.C.Z. Abilhôa, J.F.F. da Silva, W. Michelon, The potential of animal manure management pathways toward a circular economy: a bibliometric analysis, Environ. Sci. Pollut. Res. 29 (2022) 73599–73621, https://doi.org/10.1007/s11356-022-22799-y.
[56] 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.
[57] M. Samer, O. Hijazi, E. Abdelsalam, A. El-Hussein, Y. Attia, I. Yacoub, H. Bernhardt, Life cycle assessment of using laser treatment and nanomaterials to produce biogas through anaerobic digestion of slurry, Environ. Dev. Sustain. (2021) 1–14, https://doi.org/10.1007/s10668-021-01264-9.
[58] N. Verma, A. Upadhyay, P. Talwar, R. Singh, M.A. Mohamed, S.E. El-Abeid, A. Y. Ahmed, A.K. El-Attar, V. Kumar, C. Lindenberger, Effect of nanoparticles as additive for enhancing the bio methane yield in copretreated lignocellulosic biomass under solid state anaerobic co-digestion for sustainable bioeconomy in India, Biomass Bioenergy 181 (2024) 107069, https://doi.org/10.1016/j.biombioe.2024.107069.
[59] X. Wang, V. Dürr, A. Guenne, L. Mazéas, O. Chapleur, Generic role of zeolite in enhancing anaerobic digestion and mitigating diverse inhibitions: insights from degradation performance and microbial characteristics, J. Environ. Manag. 356 (2024) 120676, https://doi.org/10.1016/j.jenvman.2024.120676.
[60] M.S. Hossain, T.U. Karim, M.H. Onik, D. Kumar, M.A. Rahman, A. Yousuf, M. R. Uddin, Impact of temperature, inoculum flow pattern, inoculum type, and their ratio on dry anaerobic digestion for biogas production, Sci. Rep. 12 (2022) 6162, https://doi.org/10.1038/s41598-022-10025-1.
[61] M. Silwadi, H. Mousa, B.Y. Al-Hajji, S.S. Al-Wahaibi, Z.Z. Al-Harrasi, Enhancing biogas production by anaerobic digestion of animal manure, Int. J. Green Energy 20 (2023) 257–264, https://doi.org/10.1080/15435075.2022.2038608.
[62] M. Casallas-Ojeda, I. Cabeza, N. Sanchez, D.M. Caicedo-Concha, S. Astals, Cheese whey and dairy manure anaerobic co-digestion at psychrophilic conditions: technical and environmental evaluation, Environ. Res. 251 (2024) 118525, https://doi.org/10.1016/j.envres.2024.118525.
[63] J. Jaimes-Estévez, G. Zafra, J. Martí-Herrero, G. Pelaz, A. Morán, A. Puentes, C. Gomez, L.D. Castro, H. Escalante Hernández, Psychrophilic full scale tubular digester operating over eight years: complete performance evaluation and microbiological population, Energies 14 (2021), https://doi.org/10.3390/en14010151.
[64] J. Martí-Herrero, G. Soria-Castellón, A. Diaz-de-Basurto, R. Alvarez, D. Chemisana, Biogas from a full scale digester operated in psychrophilic conditions and fed only with fruit and vegetable waste, Renew. Energy 133 (2019) 676–684, https://doi.org/10.1016/j.renene.2018.10.030.
[65] M.A. Akindolire, H. Rama, A. Roopnarain, Psychrophilic anaerobic digestion: a critical evaluation of microorganisms and enzymes to drive the process, Renew. Sustain. Energy Rev. 161 (2022) 112394, https://doi.org/10.1016/j.rser.2022.112394.
[66] E. Rossi, I. Pecorini, A. Panico, R. Iannelli, Impact of reactor configuration and relative operating conditions on volatile fatty acids production from organic waste, Environ. Technol. Rev. 11 (2022) 156–186, https://doi.org/10.1080/21622515.2022.2139641.
[67] X. Zheng, L. Wu, Y. Chen, Y. Su, R. Wan, K. Liu, H. Huang, Effects of titanium dioxide and zinc oxide nanoparticles on methane production from anaerobic co-digestion of primary and excess sludge, J. Environ. Sci. Health Part A 50 (2015) 913–921, https://doi.org/10.1080/10934529.2015.1030279.
[68] 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 12 (2020), https://doi.org/10.3390/w12051283.
[69] D. Zhong, J. Li, W. Ma, F. Qian, Clarifying the synergetic effect of magnetite nanoparticles in the methane production process, Environ. Sci. Pollut. Res. 27 (2020) 17054–17062, https://doi.org/10.1007/s11356-020-07828-y.
[70] M. Luna-delRisco, K. Orupõld, H.-C. Dubourguier, Particle-size effect of CuO and ZnO on biogas and methane production during anaerobic digestion, J. Hazard. Mater. 189 (2011) 603–608, https://doi.org/10.1016/j.jhazmat.2011.02.085.
[71] T. Jia, Z. Wang, H. Shan, Y. Liu, L. Gong, Effect of nanoscale zero-valent iron on sludge anaerobic digestion, Resour. Conserv. Recycl. 127 (2017) 190–195, https://doi.org/10.1016/j.resconrec.2017.09.007.
[72] F. Suanon, Q. Sun, M. Li, X. Cai, Y. Zhang, Y. 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.
[73] A. Ali, R.B. Mahar, R.A. Soomro, S.T.H. Sherazi, Fe_3O_4 nanoparticles facilitated anaerobic digestion of organic fraction of municipal solid waste for enhancement

of methane production, Energy Sources Part Recovery Util, Environ. Eff. 39 (2017) 1815–1822, https://doi.org/10.1080/15567036.2017.1384866.

[74] 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 Fe_3O_4 nanoparticles on methane yield, Renew. Energy 133 (2019) 1046–1054, https://doi.org/10.1016/j.renene.2018.10.113.

[75] L.L. Li, Z.-H. Tong, C.-Y. Fang, J. Chu, H.-Q. Yu, Response of anaerobic granular sludge to single-wall carbon nanotube exposure, Water Res. 70 (2015) 1–8, https://doi.org/10.1016/j.watres.2014.11.042.

[76] J.J. Ambuchi, Z. Zhang, Y. Feng, Biogas enhancement using iron oxide nanoparticles and multi-wall carbon nanotubes, International Journal of Chemical, Molecular, Nuclear, Materials and Metallurgical Engineering 10 (2016) 1305–1311.

[77] D. Nguyen, C. Visvanathan, P. Jacob, V. Jegatheesan, Effects of nano cerium (IV) oxide and zinc oxide particles on biogas production, CESE-2014 – chall, Environ. Sci. Eng. Ser. Conf. 102 (2015) 165–171, https://doi.org/10.1016/j.ibiod.2015.02.014.

[78] Y. Liang, X. Li, J. Zhang, L. Zhang, B. Cheng, Effect of microscale ZVI/magnetite on methane production and bioavailability of heavy metals during anaerobic digestion of diluted pig manure, Environ. Sci. Pollut. Res. 24 (2017) 12328–12337, https://doi.org/10.1007/s11356-017-8832-9.

[79] G. Zhen, X. Lu, Y.-Y. Li, Y. Liu, Y. Zhao, Influence of zero valent scrap iron (ZVSI) supply on methane production from waste activated sludge, Chem. Eng. J. 263 (2015) 461–470, https://doi.org/10.1016/j.cej.2014.11.003.

[80] D. Wu, S. Zheng, A. Ding, G. Sun, M. Yang, Performance of a zero valent iron-based anaerobic system in swine wastewater treatment, J. Hazard. Mater. 286 (2015) 1–6, https://doi.org/10.1016/j.jhazmat.2014.12.029.

[81] Y. Hao, Y. Wang, C. Ma, J.C. White, Z. Zhao, C. Duan, Y. Zhang, M. Adeel, Y. Rui, G. Li, B. Xing, Carbon nanomaterials induce residue degradation and increase methane production from livestock manure in an anaerobic digestion system, J. Clean. Prod. 240 (2019) 118257, https://doi.org/10.1016/j.jclepro.2019.118257.

[82] J. Zhang, Z. Wang, Y. Wang, H. Zhong, Q. Sui, C. Zhang, Y. Wei, Effects of graphene oxide on the performance, microbial community dynamics and antibiotic resistance genes reduction during anaerobic digestion of swine manure, Bioresour. Technol. 245 (2017) 850–859, https://doi.org/10.1016/j.biortech.2017.08.217.

[83] J.J. Ambuchi, Z. Zhang, L. Shan, D. Liang, P. Zhang, Y. Feng, Response of anaerobic granular sludge to iron oxide nanoparticles and multi-wall carbon nanotubes during beet sugar industrial wastewater treatment, Water Res. 117 (2017) 87–94, https://doi.org/10.1016/j.watres.2017.03.050.

[84] E.E. Ziganshina, A.M. Ziganshin, Magnetite nanoparticles and carbon nanotubes for improving the operation of mesophilic anaerobic digesters, Microorganisms 11 (2023), https://doi.org/10.3390/microorganisms11040938.

[85] W. Yan, D. Lu, J. 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.

[86] J. Ma, Z. Yao, L. Zhao, Comprehensive study of the combined effects of biochar and iron-based conductive materials on alleviating long chain fatty acids inhibition in anaerobic digestion, Environ. Res. 239 (2023) 117446, https://doi.org/10.1016/j.envres.2023.117446.

[87] J. Yang, H. Zhang, K. Tian, Y. Zhang, J. Zhang, Novel lanthanum-iron oxide nanoparticles alleviate the inhibition of anaerobic digestion by carbamazepine through adsorption and bioaugmentation, J. Environ. Manag. 340 (2023) 117975, https://doi.org/10.1016/j.jenvman.2023.117975.

[88] T. Alkhrissat, G. Kassab, M. Abdel-Jaber, Impact of iron oxide nanoparticles on anaerobic co-digestion of cow manure and sewage sludge, Energies 16 (2023), https://doi.org/10.3390/en16155844.

[89] P. Wang, M. Yu, P. Lin, Y. Zheng, L. Ren, Effects of biochar supported nano zero-valent 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.

[90] T.A.M. Abdelwahab, M.K. Mohanty, P.K. Sahoo, D. Behera, Impact of nickel nanoparticles on biogas production from cattle manure, Biomass Convers. Biorefinery 13 (2023) 5205–5218, https://doi.org/10.1007/s13399-021-01460-7.

[91] Q. Guan, Y. Qu, Y. Zhai, W. Shi, M. Zhao, Z. Huang, W. Ruan, Enhancement of methane production in anaerobic digestion of high salinity organic wastewater: the synergistic effect of nano-magnetite and potassium ions, Chemosphere 318 (2023) 137974, https://doi.org/10.1016/j.chemosphere.2023.137974.

[92] W. Li, J. Chen, L. Pang, Y. Lu, P. Yang, Dosage effect of micron zero-valent iron during thermophilic anaerobic digestion of waste activated sludge: performance and functional community, Environ. Res. 237 (2023) 116997, https://doi.org/10.1016/j.envres.2023.116997.

[93] C. Da Silva, S. Astals, M. Peces, J. Campos, L. Guerrero, Biochemical methane potential (BMP) tests: reducing test time by early parameter estimation, Waste Manag. 71 (2018) 19–24, https://doi.org/10.1016/j.wasman.2017.10.009.

[94] P.S. Calabrò, A. Folino, M. Maesano, D. Pangallo, D.A. Zema, Exploring the possibility to shorten the duration and reduce the number of replicates in biomethane potential tests (BMP), Waste Biomass Valorization 14 (2023) 2481–2493, https://doi.org/10.1007/s12649-022-01893-9.

[95] H. Zhao, S. Cheng, C. Zhao, K. Ruan, J. Xu, X. Cheng, Effect of nano-Al_2O_3 and multi-walled carbon nanotubes on the anaerobic mono-digestion of sludge and the co-digestion of tobacco waste and sludge, RSC Adv. 13 (2023) 35621–35628, https://doi.org/10.1039/d3ra07170g.

[96] L. Rocha-Meneses, A. Hari, A. Inayat, A. Shanableh, M. Abdallah, C. Ghenai, S. Shanmugam, T. Kikas, Application of nanomaterials in anaerobic digestion processes: a new strategy towards sustainable methane production, Biochem. Eng. J. 188 (2022) 108694, https://doi.org/10.1016/j.bej.2022.108694.

[97] M.K. Devi, S. Manikandan, M. Oviyapriya, M. Selvaraj, M.A. Assiri, S. Vickram, R. Subbaiya, N. Karmegam, B. Ravindran, S. Chang, Recent advances in biogas production using Agro-Industrial Waste: a comprehensive review outlook of techno-economic analysis, Bioresour. Technol. 363 (2022) 127871, https://doi.org/10.1016/j.biortech.2022.127871.

[98] R. Pereira, A. Salvador, P. Dias, M. Pereira, M. Alves, L. Pereira, Perspectives on carbon materials as powerful catalysts in continuous anaerobic bioreactors, Water Res. 101 (2016) 441–447, https://doi.org/10.1016/j.watres.2016.06.004.

[99] S. Faisal, F. Yusuf Hafeez, Y. Zafar, S. Majeed, X. Leng, S. Zhao, I. Saif, K. Malik, X. Li, A review on nanoparticles as boon for biogas producers—nano fuels and biosensing monitoring, Appl. Sci. 9 (2018) 59, https://doi.org/10.3390/app9010059.

[100] 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. Manag. 240 (2019) 160–167, https://doi.org/10.1016/j.jenvman.2019.03.089.

[101] D.J. Batstone, J. Keller, Industrial applications of the IWA anaerobic digestion model no. 1 (ADM1), Water Sci. Technol. 47 (2003) 199–206, https://doi.org/10.2166/wst.2003.0647.

[102] C.N. Etuwe, Y.O.L. Momoh, E.T. Iyagba, Development of mathematical models and application of the modified gompertz model for designing batch biogas reactors, Waste Biomass Valorization 7 (2016) 543–550, https://doi.org/10.1007/s12649-016-9482-8.

[103] R. Mo, W. Guo, D. Batstone, J. Makinia, Y. Li, Modifications to the anaerobic digestion model no. 1 (ADM1) for enhanced understanding and application of the anaerobic treatment processes–A comprehensive review, Water Res. 244 (2023) 120504, https://doi.org/10.1016/j.watres.2023.120504.

[104] A. Donoso-Bravo, S. Pérez-Elvira, F. Fdz-Polanco, Application of simplified models for anaerobic biodegradability tests. Evaluation of pre-treatment processes, Chem. Eng. J. 160 (2010) 607–614, https://doi.org/10.1016/j.cej.2010.03.082.

[105] L.S. Avinash, A. Mishra, Comparative evaluation of Artificial intelligence based models and kinetic studies in the prediction of biogas from anaerobic digestion of MSW, Fuel 367 (2024) 131545, https://doi.org/10.1016/j.fuel.2024.131545.

[106] J. Cheng, R. Ye, J. Zhu, Y. Tang, S. Huang, D. Ge, Z. Geng, Effect of ferrite doped sludge-based catalysts on methane production in anaerobic digestion of organic solid waste, Fuel 368 (2024) 131309, https://doi.org/10.1016/j.fuel.2024.131309.

[107] B.A. Parra-Orobio, A. Donoso-Bravo, P. Torres-Lozada, Energy balance and carbon dioxide emissions comparison through modified anaerobic digestion model no 1 for single-stage and two-stage anaerobic digestion of food waste, Biomass Bioenergy 142 (2020) 105814, https://doi.org/10.1016/j.biombioe.2020.105814.

[108] L. Hassanpourmoghadam, B.A. Goharrizi, A. Torabian, E. Bouteh, B.E. Rittmann, Effect of Fe_3O_4 nanoparticles on anaerobic digestion of municipal wastewater sludge, Biomass Bioenergy 169 (2023) 106692, https://doi.org/10.1016/j.biombioe.2022.106692.

[109] E.K. Tetteh, S. Rathilal, Application of biomagnetic nanoparticles for biostimulation of biogas production from wastewater treatment, Mater, Today Proc 45 (2021) 5214–5220, https://doi.org/10.1016/j.matpr.2021.01.720.

[110] S.A. Ahmad, S.S. Das, A. Khatoon, M.T. Ansari, M. Afzal, M.S. Hasnain, A. K. Nayak, Bactericidal activity of silver nanoparticles: a mechanistic review, Mater. Sci. Energy Technol. 3 (2020) 756–769, https://doi.org/10.1016/j.mset.2020.09.002.

[111] E.K. Ünşar, A. Çığğın, A. Erdem, N. Perendeci, Long and short term impacts of CuO, Ag and CeO 2 nanoparticles on anaerobic digestion of municipal waste activated sludge, Environ. Sci. Process. Impacts 18 (2016) 277–288, https://doi.org/10.1039/C5EM00466G.

[112] Y.-J. Lee, D.-J. Lee, Impact of adding metal nanoparticles on anaerobic digestion performance–A review, Bioresour. Technol. 292 (2019) 121926, https://doi.org/10.1016/j.biortech.2019.121926.

[113] H. Sun, C. Liu, S. Ren, K. Liang, Z. Zhang, C. Su, S. Pei, M. Usman, Insights into the effects of CeO_2 nanoparticles on medium-chain carboxylates production from waste activated sludge, Sustainability 15 (2023) 6855, https://doi.org/10.3390/su15086855.

[114] G. Baek, J. Kim, C. Lee, A review of the effects of iron compounds on methanogenesis in anaerobic environments, Renew. Sustain. Energy Rev. 113 (2019) 109282, https://doi.org/10.1016/j.rser.2019.109282.

[115] J. Bosch, A. Fritzsche, K.U. Totsche, R.U. Meckenstock, Nanosized ferrihydrite colloids facilitate microbial iron reduction under flow conditions, Geomicrobiol. J. 27 (2010) 123–129, https://doi.org/10.1080/01490450903456707.

[116] C.-S. He, R.-R. Ding, Y.-R. Wang, Q. Li, Y.-X. Wang, Y. Mu, Insights into short-and long-term effects of loading nickel nanoparticles on anaerobic digestion with flocculent sludge, Environ. Sci. Nano 6 (2019) 2820–2831, https://doi.org/10.1039/C9EN00628A.

[117] B.A. Parra-Orobio, A. Donoso-Bravo, J.C. Ruiz-Sánchez, K.J. Valencia-Molina, P. Torres-Lozada, Effect of inoculum on the anaerobic digestion of food waste accounting for the concentration of trace elements, Waste Manag. 71 (2018) 342–349, https://doi.org/10.1016/j.wasman.2017.09.040.

[118] 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.
[119] H. Liu, Y. Xu, X. Chen, X. Wang, H. Wang, X. Dai, MOF-based materials facilitate efficient anaerobic digestion of organic wastes: integrating substrate bioavailability and microbial syntrophism, Front. Environ. Sci. Eng. 18 (2024) 105, https://doi.org/10.1007/s11783-024-1865-7.
[120] B.A. Parra-Orobio, M.N. Cruz-Bournazou, P. Torres-Lozada, Single-stage and two-stage anaerobic digestion of food waste: effect of the organic loading rate on the methane production and volatile fatty acids, water, Air. Soil Pollut. 232 (2021) 105, https://doi.org/10.1007/s11270-021-05064-9.
[121] R. Wang, N.A. Al-Dhabi, Y. Jiang, X. Dai, R. Li, W. Tang, R. Guo, S. Fu, Effect of nano zero-valent iron on the anaerobic digestion of food waste: performance and mechanism, Fuel 366 (2024) 131342, https://doi.org/10.1016/j.fuel.2024.131342.
[122] J. Cheng, J. Hua, T. Kang, B. Meng, L. Yue, H. Dong, H. Li, J. Zhou, Nanoscale zero-valent iron improved lactic acid degradation to produce methane through anaerobic digestion, Bioresour. Technol. 317 (2020) 124013, https://doi.org/10.1016/j.biortech.2020.124013.
[123] M.J. McInerney, J.R. Sieber, R.P. Gunsalus, Syntrophy in anaerobic global carbon cycles, Curr. Opin. Biotechnol. 20 (2009) 623–632, https://doi.org/10.1016/j.copbio.2009.10.001.
[124] Z.M. Summers, H.E. Fogarty, C. Leang, A.E. Franks, N.S. Malvankar, D.R. Lovley, Direct exchange of electrons within aggregates of an evolved syntrophic coculture of anaerobic bacteria, Science 330 (2010) 1413–1415, https://doi.org/10.1126/science.1196526.
[125] K. Igarashi, E. Miyako, S. Kato, Direct interspecies electron transfer mediated by graphene oxide-based materials, Front. Microbiol. 10 (2020) 3068, https://doi.org/10.3389/fmicb.2019.03068.
[126] D.R. Lovley, Syntrophy goes electric: direct interspecies electron transfer, Annu. Rev. Microbiol. 71 (2017) 643–664, https://doi.org/10.1146/annurev-micro-030117-020420.
[127] 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) 8982–8989, https://doi.org/10.1039/C2EE22459C.
[128] J. Zhang, Y. Lu, Conductive Fe_3O_4 nanoparticles accelerate syntrophic methane production from butyrate oxidation in two different lake sediments, Front. Microbiol. 7 (2016) 1316, https://doi.org/10.3389/fmicb.2016.01316.
[129] S. Kato, K. Hashimoto, K. Watanabe, Microbial interspecies electron transfer via electric currents through conductive minerals, Proc. Natl. Acad. Sci. 109 (2012) 10042–10046, https://doi.org/10.1073/pnas.1117592109.
[130] P. Jadhav, Z.B. Khalid, A.W. Zularisam, S. Krishnan, M. Nasrullah, The role of iron-based nanoparticles (Fe-NPs) on methanogenesis in anaerobic digestion (AD) performance, Environ. Res. 204 (2022) 112043, https://doi.org/10.1016/j.envres.2021.112043.
[131] R.K. Thauer, Methyl (Alkyl)-coenzyme M reductases: nickel F-430-containing enzymes involved in anaerobic methane formation and in anaerobic oxidation of methane or of short chain alkanes, Biochemistry 58 (2019) 5198–5220, https://doi.org/10.1021/acs.biochem.9b00164.
[132] H. Park, P.A. Johnson, The development and evaluation of chitosan-coated enzyme magnetic nanoparticles for cellulose hydrolysis, Front. Chem. Eng. 6 (2024) 1479798, https://doi.org/10.3389/fceng.2024.1479798.
[133] P. Ghofrani-Isfahani, H. Baniamerian, P. Tsapekos, M. Alvarado-Morales, T. Kasama, M. Shahrokhi, M. Vossoughi, I. Angelidaki, Effect of metal oxide based TiO_2 nanoparticles on anaerobic digestion process of lignocellulosic substrate, Energy 191 (2020) 116580, https://doi.org/10.1016/j.energy.2019.116580.
[134] A. El Nemr, M.A. Hassaan, M.R. Elkatory, S. Ragab, A. Pantaleo, Efficiency of Fe_3O_4 nanoparticles with different pretreatments for enhancing biogas yield of macroalgae *Ulva intestinalis* Linnaeus, Molecules 26 (2021) 5105, https://doi.org/10.3390/molecules26165105.
[135] J. Zhou, H. Zhang, J. Liu, L. Gong, X. Yang, T. Zuo, Y. Zhou, J. Wang, X. You, Q. Jia, Effects of Fe_3O_4 nanoparticles on anaerobic digestion enzymes and microbial community of sludge, Environ. Technol. 44 (2023) 68–81, https://doi.org/10.1016/j.biombioe.2022.106692.
[136] P.M. Thanh, B. Ketheesan, Z. Yan, D. Stuckey, Trace metal speciation and bioavailability in anaerobic digestion: a review, Biotechnol. Adv. 34 (2016) 122–136, https://doi.org/10.1016/j.biotechadv.2015.12.006.
[137] M.A. Voelklein, R. O'Shea, A. Jacob, J.D. Murphy, Role of trace elements in single and two-stage digestion of food waste at high organic loading rates, Energy 121 (2017) 185–192, https://doi.org/10.1016/j.energy.2017.01.009.
[138] T. Zhang, P.-L. Tremblay, Graphene: an antibacterial agent or a promoter of bacterial proliferation? iScience 23 (2020) 101787 https://doi.org/10.1016/j.isci.2020.101787.
[139] P.-H. Hsieh, Y.-C. Lai, K.-Y. Chen, C.-H. Hung, Explore the possible effect of TiO_2 and magnetic hematite nanoparticle addition on biohydrogen production by *Clostridium pasteurianum* based on gene expression measurements, Int. J. Hydrogen Energy 41 (2016) 21685–21691, https://doi.org/10.1016/j.ijhydene.2016.06.197.
[140] M.T. Valentin, G. Luo, S. Zhang, A. Białowiec, Direct interspecies electron transfer mechanisms of a biochar-amended anaerobic digestion: a review, Biotechnol. Biofuels Bioprod. 16 (2023) 146, https://doi.org/10.1186/s13068-023-02391-3.
[141] T.A. Aragaw, F.M. Bogale, B.A. Aragaw, Iron-based nanoparticles in wastewater treatment: a review on synthesis methods, applications, and removal mechanisms, J. Saudi Chem. Soc. 25 (2021) 101280, https://doi.org/10.1016/j.jscs.2021.101280.
[142] D. Yellezuome, X. Zhu, Z. Wang, R. Liu, Mitigation of ammonia inhibition in anaerobic digestion of nitrogen-rich substrates for biogas production by ammonia stripping: a review, Renew. Sustain. Energy Rev. 157 (2022) 112043, https://doi.org/10.1016/j.rser.2021.112043.
[143] H.-L. Fan, S.-F. Zhou, W.-Z. Jiao, G.-S. Qi, Y.-Z. Liu, Removal of heavy metal ions by magnetic chitosan nanoparticles prepared continuously via high-gravity reactive precipitation method, Carbohydr. Polym. 174 (2017) 1192–1200, https://doi.org/10.1016/j.carbpol.2017.07.050.
[144] J.-H. Park, H.-J. Kang, K.-H. Park, H.-D. Park, Direct interspecies electron transfer via conductive materials: a perspective for anaerobic digestion applications, Bioresour. Technol. 254 (2018) 300–311, https://doi.org/10.1016/j.biortech.2018.01.095.
[145] D. Xia, X. Shi, K. Chen, A. Hao, Y. Iseri, Understanding the mechanisms behind the antibacterial activity of magnesium hydroxide nanoparticles against sulfate-reducing bacteria in sediments, Sci. Rep. 14 (2024) 21831, https://doi.org/10.1038/s41598-024-72516-7.
[146] P. Wang, X. Li, Y. Li, Y. 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.
[147] A. Grosser, A. Grobelak, A. Rorat, P. Courtois, F. Vandenbulcke, S. Lemière, R. Guyoneaud, E. Attard, P. Celary, Effects of silver nanoparticles on performance of anaerobic digestion of sewage sludge and associated microbial communities, Renew. Energy 171 (2021) 1014–1025, https://doi.org/10.1016/j.renene.2021.02.127.
[148] M. Kaur, P.C. Sahoo, M. Kumar, S. Sachdeva, S. Puri, Effect of metal nanoparticles on microbial community shift and syntrophic metabolism during anaerobic digestion of *Azolla microphylla*, J. Environ. Chem. Eng. 9 (2021) 105841, https://doi.org/10.1016/j.jece.2021.105841.
[149] A. Córdova-Lizama, C. Carrera-Figueiras, A. Palacios, P. Castro-Olivera, J. Ruiz-Espinoza, Improving hydrogen production from the anaerobic digestion of waste activated sludge: effects of cobalt and iron zero valent nanoparticles, Int. J. Hydrogen Energy 47 (2022) 30074–30084, https://doi.org/10.1016/j.ijhydene.2022.06.187.
[150] A. Ancy, M. Lazar, A.S. Chandran, M. Ushamani, Development of ecofriendly and sustainable bioplastics from cassava starch: tailoring the properties using nanoparticles, Sustain. Chem. Pharm. 37 (2024) 101377, https://doi.org/10.1016/j.scp.2023.101377.
[151] P. Rodríguez, A. Cerda, X. Font, A. Sánchez, A. Artola, Valorisation of biowaste digestate through solid state fermentation to produce biopesticides from *Bacillus thuringiensis*, Waste Manag. 93 (2019) 63–71, https://doi.org/10.1016/j.wasman.2019.05.026.
[152] I.A. Cruz, W. Chuenchart, F. Long, K. Surendra, L.R.S. Andrade, M. Bilal, H. Liu, R. T. Figueiredo, S.K. Khanal, L.F.R. Ferreira, Application of machine learning in anaerobic digestion: perspectives and challenges, Bioresour. Technol. 345 (2022) 126433, https://doi.org/10.1016/j.biortech.2021.126433.