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Mini-Review: Nanoparticles for Enhanced Biogas Upgrading

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Abstract

This mini-review is intended to explore the innovative applications of nanoparticles in biogas upgrading, emphasizing their capacity to enhance biogas quality. Numerous studies underscore how nanoparticles, when applied during anaerobic digestion, can boost not only the quantity but also the quality of the produced biogas, leading to reduce significantly the concentration of hydrogen sulfide or even to remove it completely. Moreover, nanoparticles are proving to be excellent alternatives as adsorbent materials, achieving up to 400 mg_{H2S} g^{-1} nanoparticles. In addition, new studies are exploring the application of nanoparticles to increase the efficiency of biological treatments thanks to their unique features. This review also emphasizes the potential benefits and addresses the challenges that need to be overcome for these

technologies to reach their full potential, ultimately contributing to the development of a sustainable and environmentally friendly energy landscape.

Keywords

Biogas upgrading, Nanoparticles, Biomethane, Biogas purification nanoparticles, Hydrogen sulfide removal

Highlights

- Metal and oxide metal nanoparticles are the most used for biogas upgrading;
- Nanoparticles in digestors can completely remove hydrogen sulfide from biogas;
- Nanoparticles can adsorb up to 400 mg_{H2S} g^{-1};
- The addition of nanoparticles could increase the efficiency of biological treatments;
- No information on the cost effectiveness of biogas upgrading by metal nanoparticles

1.1 Introduction

The extensive release of carbon dioxide (CO_2), with an estimated emission rate around 1000 kg s^{-1} (Adnan et al., 2019; Fifth Assessment Report — IPCC, 2014), underscores the need for investing in renewable energy solutions. Nowadays, bioenergy constitutes approximately 70% of all primary renewable energy, playing a crucial role for power and heat generation since its flexibility and constant and predictable electricity supply sets it apart from other renewable energies like wind, solar, hydro, or tidal power (Röder and Welfle, 2019; Abanades et al., 2022).

Anaerobic digestion (AD) to produce biogas is one of the most used technologies to convert biomasses into bioenergy, with a world amount of biogas plant capacity of about 120 GW at the end of 2019 (Kabeyi and Olanrewaju, 2022). This makes it a crucial contribution to clean energy production, whose demand will increase more and more, given the predicted global population reaching 10 billion by 2050 (Bauer et al., 2013; Peccia and Westerhoff, 2015). AD can convert biomass and organic wastes such as sewage sludge, municipal organic waste, and animal farm manure into energy through the production of biogas and digestate. The circularity of the system relies on the reuse of digestate, particularly in the agricultural sector where it serves as an amendment (Panuccio et al., 2019). However, for agricultural use, an appropriate assessment is required to ensure the compliance of digestate quality with the standards in force (Samoraj et al., 2022). To address this challenge, new applications for digestate must be explored to increase the sustainability of the process. For example, Maroušek et al., (2023a) used digestate from maize and manure AD for the production of charcoal. The resulting coal, activated with iron chloride (III), was then employed to bind phosphorus from a wastewater treatment plant, and the ferric phosphate-rich coal was tested as a cement substitute in concrete production. Stehel et al. (2018) employed pyrolyzed digestate as an additive to enhance AD, and also explored its potential for wall finishing inside the buildings. This investigation aimed to assess the material capacity to capture atmospheric pollutants and contribute to improve indoor air quality. The outcomes from both applications have demonstrated significant promise, indicating the positive impact of utilizing pyrolyzed digestate in these roles.

These diverse applications aim to ensure not only environmental and people-friendly processes but also economic sustainability for producers, with the potential for additional revenue from by-product sale (Pavolová et al., 2021).

Biogas is a mixture of different gases that mainly includes methane (CH_4, 50–75%), CO_2, (25-50%), and other trace gases such as hydrogen sulfide (H_2S, 0–3%) (Angelidaki et al., 2018; Goswami et al., 2010). H_2S and CO_2 are the most problematic components: the first is a toxic and corrosive compound, while the second one reduces the biogas calorific power. Hence, to optimize the use of biogas as fuel, it is necessary to upgrade the raw biogas, reducing the concentration of the contaminants, to obtain biomethane (CH_4 95-98%), which can be a substitute for natural gas and can be fed into the gas network (Ryckebosch et al., 2011). Since the technologies for upgrading biogas represent one of the major costs in the production of biomethane, it is necessary to keep the costs for upgrading as low as possible (Bose et al.,2022). Nowadays, the transformation of biogas into biomethane is still challenging and its economic profitability is unknown except for local or regional studies. In particular, González-Arias et al., (2021) highlighted the non-economic sustainability of biogas upgrading for small plants (100-250 m^3 h^{-1}) in the region of Brandeburg (Germany) and the consequent need for additional economic efforts or subsidies to achieve profitability. The same study states that prices for biomethane should be higher than the current ones to make small businesses competitive. This, however, would decrease the competitiveness of biomethane towards fossil fuels, which today are the most used source for energy production (Vochozka et al., 2020). To address this challenge, the most viable solution appears to be reducing the cost of biomethane production (Bose et al., 2022).

Nanotechnology could play an essential role in the removal of contaminants from biogas potentially reducing upgrading costs and increasing process efficiency. Nanomaterials in various shapes/morphologies, such as nanoparticles (NPs), function as adsorbents and catalysts, and they are already used for the detection and removal of gases (sulfur dioxide, carbon monoxide, nitrogen oxides, etc.), inorganic (arsenic, manganese, nitrate, heavy metals, etc.) and organic pollutants (aliphatic and aromatic hydrocarbons) (Khin et al., 2012). Moreover, they can be combined with existing biogas treatment technology to improve performance and reduce costs. The properties of NPs make them optimal for the treatment and elimination of CO_2 and gas traces such as H_2S present in raw biogas due to their adsorption capacity, catalytic properties, and chemical reactivity (Khin et al., 2012).

This review aims to analyze the different studies dealing with the applications of NPs for biogas upgrading, highlighting the results obtained and providing a general framework. Based on the collected information, this mini-review would try to understand if the buzz around NPs for biogas upgrading is justified.

1.2 State-of-the-art: upgrading technologies and nanoparticles

Contaminant removal methods for biomethane upgrading could be divided into ex-situ and in-situ technologies, where ex-situ is performed outside the digester, after biogas generation. In contrast, in-situ is performed in the digester (Ghimire et al., 2021). In-situ methods are mainly used to avoid the presence of H_2S in the biogas (Petersson and Wellinger, 2008). A typical example is iron chloride (II) insertion to the digester (H_2S precipitate as iron sulfide or sulfur) or 6-12% air/ 2-6% oxygen injection for H_2S oxidation to sulfur. However, these two methods pose challenges. In both cases, it is difficult to quantify the correct amount of iron chloride and oxygen to be fed into the digester, with the risk of under- or over-dosing (Ryckebosch et al., 2011). Furthermore, the utilization of iron chloride in the digestor may result in the presence of iron compounds in the digestate, potentially causing phosphorus blockage in the soil and consequently diminishing its soil fertilizing properties (Maroušek et al., 2022a).

Ex-situ methods include indeed the most used upgrading technologies since they are more effective and easier to be applied (Ghimire et al., 2021). They can be classified into two groups according to their working mechanism: the conventional physicochemical treatments, which still dominate the market, and the biological ones (Ghimire et al., 2021). These last methods are raising considerable interest as they have the same or even higher efficiency than the physicochemical methods (> 99%) but lower operating costs. They do not need catalysts and do not generally produce secondary streams that must be specifically treated. A typical example of biological treatment is the use of microalgae, where these microorganisms fix CO_2 from biogas through the photosynthetic process (Luo and Angelidaki, 2013). Consortia of microalgae and sulfur-oxidizing bacteria are also used to remove CO_2 and H_2S (Bahr et al., 2014). However, it should be stressed that the economics of using microalgae can be complex to be defined, and, in this respect, studies are still at early stages (Maroušek et al., 2023b; Maroušek et al., 2023c). It will therefore be necessary to carry out further studies and a careful cost-benefit analysis to assess the economic feasibility of this technology.

Bacteria are also used for biogas upgrading: sulfide-oxidizing microorganisms can remove H_2S, homoacetogenic, acetogenic, or methanogenic bacteria are able to generate valuable compounds or additional CH_4 from exogenous hydrogen (H_2) and CO_2 from biogas (Luo and Angelidaki, 2013). Also in this case, basic and applied research for optimization are generally still required (Ghimire et al., 2021). Physicochemical treatments, instead, are established and involve commonly used technologies which represent more than 85% of the whole market (Statistical report of the European biogas association 2018, 2018). However, they have a high-energy demand (as pressing swig adsorption that requires ~ 0.25 kWh Nm^{-3} of raw biogas), high investment costs (e.g., membrane separation 3,500-7,500 € $(m^3\ h^{-1})^{-1}$, activated carbon up to \$ 1,500 ton^{-1}) (Baena-Moreno et al., 2020; Inyang and Dickenson, 2015), or use chemicals that need to be regenerated or eliminated (as chemical scrubbing) (Angelidaki et al., 2018; Awe et al., 2017; Petersson and Wellinger, 2008; Ryckebosch, et al., 2011; Sun et al., 2015). Methods combining physicochemical and biological technologies have also been developed but are still uncommon (Ghimire et al., 2021). These are the reasons why research is still necessary to reduce operation costs and make eco-friendly technologies more affordable.

Concerning NPs, the International Organization for Standardization (ISO) defined them as discrete nano-objects where all three cartesian dimensions are below 100 nm (Joudeh and Linke, 2022). Many other authors also included in the class of NPs nano-objects with at least one submicrometric dimension. However, it is believed that such wording may be misleading, and the term nanomaterials is a more suitable definition for nano-objects with at least one dimension in the range of the nanometric scale.

Therefore, the ISO definition will be the definition of NPs in this review, according to Joudeh and Linke (2022).

Also, many different criteria are used regarding the classification, such as origin and morphology.

Based on chemical composition, NPs are generally placed into four classes (Khan and Hossain, 2022):

1. Inorganic nanoparticles: the typical examples of this class are metal and oxide, ceramic, and semiconductor NPs:

    - Metallic and oxide nanoparticles: metallic NPs are submicron scale entities made of pure metals e.g., gold (Au), platinum (Pt), cobalt (Co), copper (Cu), silver (Ag), nickel (Ni), titanium (Ti), zinc (Zn), cerium (Ce), iron (Fe), and thallium (Tl), or of metals combined with oxygen such as zinc oxide (ZnO), iron oxides (FeO, Fe_2O_3, Fe_3O_4), aluminium oxide (Al_2O_3), cobalt oxide (CoO), copper oxide (CuO), magnesium oxide (MgO), nickel oxide (NiO), titanium oxide (TiO_2), cerium oxide (CeO_2), and zirconium dioxide (ZrO_2) (Manzoor et al., 2021).
    - Semiconductor nanoparticles: Semiconductor materials have electrical conductivity in between conductors and insulators. They have an electron bandgap smaller than insulators and larger than conductors. Even though there is no strict quantitative definition; generally, materials with a bandgap of 3.5 eV or less are considered semiconductors. This group includes silicon (Si), germanium (Ge), zinc (ZnS, ZnO), cadmium (CdS, CdSe, CdTe), gallium (GaN, GaP, GaAs), and iridium compounds (InP, and InAs) (Khan and Hossain, 2022).
    - Ceramic nanoparticles: Ceramic NPs are primarily made up of oxides of silicon (SiO_2), aluminium (Al_2O_3), titanium (TiO_2), or zirconium (ZrO_2). Others include carbides of silicon (SiC), phosphates and carbonates of metals, and metalloids such as calcium (Sun et al., 2015).
2. Carbon-based nanoparticles: NPs are included made from carbon atoms such as fullerenes, carbon black NPs, nanodiamonds, and carbon-based quantum dots (Joudeh and Linke, 2022; Patel et al., 2019).
3. Carbon encapsulated nanoparticles: NPs combining carbon and metal have enhanced properties and reactivity. Many different organic matrices can be used as carbon source, for example green residues, waste products and biomasses (Calderon et al., 2018; Mantovani et al., 2022).

4. Organic nanoparticles: This class comprises NPs made of proteins, carbohydrates, lipids, polymers, or other organic compounds. The most prominent examples of this class are dendrimers, liposomes, micelles, and protein complexes such as ferritin. They are mainly used in pharmaceutical and medical research or studied as drug carriers and, for these reasons, will not be considered further in this review (Khan and Hossain, 2022).

1.3 In-situ upgrading: the role of nanoparticles in anaerobic digestion

NPs for biogas upgrading can be applied both in-situ and ex-situ. In the first case, NPs are inserted inside the digester during AD. In the second case, NPs can be used as adsorbent materials for the creation of new filtering systems, (Su et al., 2018) or to improve both economically available technologies, such as activated carbon filtration (Kim et al., 2012) or scrubbing (Ma and Zou, 2018), and emergent technologies, such as biological treatments with bacteria (Wu et al., 2023) and microalgae (Vargas-Estrada, et al., 2023a).

The addition of NPs to the digester to improve biogas yield is mainly studied since it can increase biogas production by 8–28% (Rocha-Meneses et al., 2022).

Metallic and metal oxide NPs represent the most significant portion of nanomaterials utilised to enhance the performance of AD processes (Rocha-Meneses et al., 2022). However, not all metallic NPs can improve biogas production: some NPs, such as Ag and Ti, have antibacterial properties that lead to slower microbial growth, reduce biogas yield, and inhibit enzymatic reactions during the AD process. On the other hand, Fe, Ni, and Co are the most studied and promising elements (Choong et al., 2016).

There are many reasons why these NPs seem to enhance biogas and CH_4 yield: Feng et al. (2014) suggest that metal NPs could enhance the activities of major enzymes related to hydrolysis, acidification, and methanogenesis. This can be explained by the fact that the metal NPs in the digestate contribute micronutrients such as Fe, Co, and Ni, which are essential constituents of cofactors and enzymes

(Jatunarachchi et al., 2006). Increased enzyme activity could decrease the time required to reach peak production and increase total CH_4 production.

As an example, Abdelsalam et al. (2017) analysed the impact of metal NPs (Co, Ni, Fe, and Fe_3O_4) on the biogas production of fresh raw manure. The results obtained in this study showed that using NPs decreased the lag phase, reduced the time to achieve the peak of biogas and CH_4 production, and biostimulated the methanogenic archaea increasing their activity. The authors attributed the results mainly to the metallic ions absorbed by the anaerobic microorganisms as growth elements.

Metal NPs could also reduce the oxidation-reduction potential when added into anaerobic systems, creating a more favourable environment for the anaerobic biological process, which requires an oxidation-reduction potential between -100 and -300 mV (Jatunarachchi et al., 2006). This leads, for example, to an enhancement in acetate production during acetogenesis, which requires an oxidation-reduction potential around -300 MV (Ren et al., 2007), with a consequent increase in the biomethane produced through autotrophic methanation.

Lastly, metal NPs were shown to act as direct interspecies electron transfer (Jadhav et al., 2022). This process promotes rapid electron donation/acceptance of microbes that produce more biogas during the AD. Many authors observed that adding metal and metal oxide NPs not only increases the biogas yield but also can improve its quality. These NPs indeed can reduce the amount of H_2S produced, allowing time and cost savings in ex-situ upgrading treatments (Abdelfattah Mohammed Abdelwahab et al. 2021a; Carpenter et al., 2015; Su et al., 2012).

The mechanisms and capacity to remove H_2S seem closely related to the type and quantity of NPs used. Su et al. (2012) observed a reduction of the concentration of H_2S in biogas by 98% compared to the control by adding 800 mg L^{-1} in weight (2g in 200g of dewatered biomass) of NPs of zero-valent iron (nZVI). This was attributed to the reducing power of nZVI, as follows:

$$H_2S + Fe^0 \rightarrow H_2 + FeS \quad (1)$$

However, the authors suggest that it may not be the only pathway for the abatement of H_2S during sludge AD. The high presence of iron oxides due to the reaction of nZVI with water (2) present in the digester, could lead also to (Yan et al., 2010):

$$Fe^0 + 2H_2O \rightarrow FeOOH + 1.5H_2 \quad (2)$$

$$2FeOOH + 3H_2S \rightarrow 2FeS + 1/8S_8 + 4H_2O \quad (3)$$

Oxidation product pyrite (FeS_2) is also cited for sulfide reaction (4):

$$2FeOOH + 3H_2S \rightarrow FeS_2 + FeS + 4H_2O \quad (4)$$

According to other papers, high concentrations of nZVI inhibit sulfate-reducing bacteria, which are responsible for producing H_2S during the AD process (Kaksonen and Puhakka, 2007). For example, Kumar et al. (2014) reported 1 g L^{-1} of nZVI as an inhibitory concentration for sulfate-reducing bacteria activity. Also, other metallic NPs could inhibit SBR activity, as reported by Liu et al. (2021), who found a decrease in H_2S production in the bioreactor at 200 mg L^{-1} Ni NPs due to sulfate-reducing bacteria inhibition. However, these concentrations are high, especially in the case of Fe. Hence, the inhibition could happen only when a high dosage is used.

Gran et al. (2022) studied the effects of 100 mg L^{-1} of NiO, CoO, and Fe_3O_4 NPs on a mixture of primary and waste-activated sludge from municipal wastewater treatment plants. The author found that H_2S reduction in digestors treated with NiO, CoO, and Fe_3O_4 was 18%, 13%, and 28%, respectively, lower than in the control. H_2S removal was probably due to sulfide precipitation as metal sulfide (NiS, CoS, and FeS) in the digesters.

Abdelfattah Mohammed Abdelwahab et al. (2021a) also found a 48% H_2S decrease by adding 2 mg L^{-1} Ni NPs to the digester and attributed it to metal sulfide formation.

The main mechanisms for the decrease in H_2S concentration in biogas would thus be related mainly to chemical precipitation, even if the chemical and physical properties of the NPs greatly influence the results obtained. The data might also be affected by the different characteristics of the digested substrate (Abdelfattah Mohammed Abdelwahab et al., 2021a).

Many authors also tested different combinations and concentrations of NPs inside the digester to achieve better removal capacities. As an example, Hassanein et al. (2019) found 100% removal of H_2S using a mixture at high concentrations (>100 mg L^{-1}) of Fe, Ni, and Co NPs. This was probably due to the combination of different removal mechanisms given by the different particles. In this case, also inhibition of sulfate-reducing bacteria could occur due to high dosage.

However, it could be necessary to consider any toxicity that may be caused by the combination of different NPs, especially at high concentrations, since detailed studies on toxicity are lacking (Rocha-Meneses et al., 2022). Further, NPs in digestate could hinder its possible reuse and valorisation and therefore a careful analysis should be conducted on the effects of NPs-enriched digestate on agricultural soils and crops (Beisl et al., 2022; Lee and Lee, 2019). Table 1 summarises some articles dealing with the effect of metal NPs on H_2S concentration in biogas from AD.

*Table 1: Summary of literature on the effect of metal NP on H_2S concentration in biogas (in situ upgrading). H_2S removal percent is calculated as 100·(1- H_2S NPs treatment/H_2S control). *Average removal of first nine days; **2g in 200g of dewatered biomass; *** calculated as reduction compared to control 100·(H_2S control-H_2S treat)/H_2S treat*

Biomass	**Metal NPs**	**Dose (mg L^{-1})**	**H_2S Removal percent**	**Time and temperature**	**References**
cattle manure	Ni	1	14%	30 days at 33±0.5°C	Abdelfattah Mohammed Abdelwahab et al. (2021a)
		2	48%		
		4	34%		
cattle manure	Fe, Ni, Co	30 Fe, 2 Ni and 1 Co	24%	15 days at 33±0.5°C	Abdelfattah Mohammed Abdelwahab et al. (2021b)
		30 Fe, 2 Ni, 0 Co	26%		
		30 Fe, 0 Ni, 1 Co	15%		
		0 Fe, 2 Ni, 1 Co	3%		

cattle manure	Fe	15	45%	30 days at 33±0.5°C	Abdelfattah Mohammed Abdelwahab et al. (2020)
		30	49%		
		60	53%		
cattle manure	Fe_2O_3	100	34%	30 days at 38°C	Farghali et al. (2020)
		500	46%		
		1000	54%		
cattle manure	Fe_2O_3	20	33%*-88%	30 days at 38°C	Farghali et al. (2019)
		100	36%*-97%		
	TiO_2	100	35%*- 98%		
		500	36%*-98%		
	Fe_2O_3 and TiO_2	20 Fe_2O_3 100 TiO_2	42%*-99%		
		100 Fe_2O_3 500 TiO_2	37%*-84%		
primary sludge and waste activated sludge of WWTP	Ni, CoO, Fe_3O_4 combinated	100 NiO,100 CoO,100 Fe_3O_4	53%	35 ± 1 °C	Gran et al. (2022)
		1 NiO ,1 CoO,100 Fe_3O_4	33%		
	Fe_3O_4	100	28%		
	NiO	100	18%		
	Co	100	13%		
poultry litter	Fe, Ni, and Co combinated	1000 Fe, 120 Ni, and 54 Co	100% in first 28 and 34 days after NPs addiction. 56% avarage reduction	270 days. First addiction of NPs at day 82 and second at day 202. 35 ± 0.5 °C	Hassanein, et al. (2021)
poultry litter	Fe, Ni, and Co combinated	1000 Fe, 120 Ni, and 54 Co	100%	79 days, 35°C	Hassanein et al. (2019)
		400 Fe, 48 Ni, and 21.6 Co	72%		
		200 Fe, 24 Ni, and 10.8 Co	41%		
		100 Fe, 12 Ni, and 5.4 Co	12%		
Waste-activated sludge from WWTP	nano zero valent iron	800**	98%***	17 days at 37°C	Su et al. (2012)

NPs inside the reactor could also affect the CO_2 produced during AD. Carpenter et al. (2015) found that the addition of 2.5 and 5.0 g L^{-1} nZVI in a digester (fed on biomass from the treatment of brewery wastewater) can decrease the amount of CO_2 released from the bioreactor by approximately 58%, increasing the CH_4 production by 28%. The authors suggest that nZVI can undergo an oxidation/reduction reaction with CO_2 and water to produce iron carbonate ($FeCO_3$) and H_2 according to the following reaction:

$$Fe^0 + CO_2 + H_2O \rightarrow FeCO_3(s) + H_2 \qquad (5)$$

nZVI can also enhance the growth of H_2-utilizing microorganisms, including hydrogenotrophic methanogens, as reported by Feng et al. (2014). It has also been reported that the oxidation of nZVI was beneficial for the growth of CO_2-consuming microorganisms (Wei et al., 2018). These factors could facilitate the conversion of CO_2 into CH_4, reducing the amount of CO_2 in the biogas and increasing biomethane concentration.

However, no other authors reported data on the decrease of CO_2, as most papers only provide biogas and CH_4 yield; hence, it is difficult to draw a conclusion.

While numerous studies have explored the application of NPs in AD, there is a notable scarcity of information concerning the economic aspects. Given the substantial costs linked to nanoparticle synthesis, it becomes crucial to analyse expenses related to their production, material losses during the synthesis process, and potential recovery from effluents, if feasible (Kumar et al., 2021). It is essential to grasp the costs linked to using NPs, along with any extra income from better biogas production and quality. Equally important is a thorough examination of the environmental impact through life cycle analysis studies, particularly if using NPs could affect the use of digestate.

1.4 Ex-situ: physicochemical treatments using nanoparticles

NPs can also be used as an adsorbent material, especially for H_2S removal, due to their efficiency and relatively low cost. In most cases, metal or metal oxide NPs are used to create adsorbent fixed bed reactors, through which the biogas is flushed and purified. Again, the results obtained by the different authors differ greatly depending on the material used.

Su et al. (2018) treated biogas with high H_2S concentration (10,000 ppm) using a custom-designed quartz fixed-bed reactor in which Fe NPs were inserted. The results showed that the H_2S removal capacity was 488.95 mg H_2S g $nZVI^{-1}$ at 250°C, while lower temperatures led to lower capacity. In the case of 250°C treatment, the main pathway for H_2S removal should differ from the previously reported one (reactions 2, 3, and 4) due to the absence of H_2O and the high temperature. The X-ray photoelectron spectrometry peak deconvolution of sulfur showed the presence of mono-sulfide (S^{2-}) and disulfide (S_2^{2-}) in the product. It was proposed that the main path for H_2S removal by nZVI at elevated temperatures could result in the reaction of nZVI and could be as follows:

$$H_2S + Fe^0 \rightarrow H_2 + FeS \qquad (6)$$

$$2\ H_2S + Fe^0 \rightarrow 2\ H_2 + FeS_2 \qquad (7)$$

Li et al. (2020) obtained similar results and conclusions with Fe NPs synthesized using extracts of dark tea leaves as a reducing agent (DT-Fe NPs) and further thermal treatment at different temperatures (300°C - 800°C). The results showed that the best H_2S removal capacity was 408.30 mg H_2S g $nZVI^{-1}$ when DT-Fe NPs were thermally treated at 400°C. The removal experiments were conducted at 250°C using a custom-designed fixed-bed reactor with an H_2S inlet concentration of 10,000 ppm. The use of tea leaf extracts allows for reducing the economic and environmental costs of nZVI synthesis with expensive chemical agents (sodium borohydride). However, in both cases, the process was carried out in fixed-bed reactors at high working temperatures, thus involving high operating costs.

Mamun and Torii (2015) obtained 95% H_2S removal at pH 6 (H_2S starting concentration in biogas 140 ppm) fluxing biogas through a vessel filled with nZVI-NPs and water suspension at room temperature. In this case, the use of an aqueous solution with NPs probably led to different reaction mechanisms similar to those already reported in reactions (2), (3), and (4). This could be a starting point for a new investigation to decrease energy demand and operating costs.

Van-Pham et al. (2022) also studied a method for removing H_2S from biogas at room temperature using hydroxyapatite NPs (HA) combined with ZnO (ZnO/HA). The results showed a removal capacity of 26.3 mg S g^{-1} with the sorbent ZnO (15 wt%)/HA NPs when a synthetic biogas with an H_2S concentration of 1,540 ppmv was passed through a U-shaped Pyrex glass tube filled with NPs. This value was the highest ever achieved for ZnO/HA, and the process did not require high temperature. However, the H_2S capacity removal was much lower than reported by Su et al. (2018) and Li et al. (2020). The reactions of H_2S on ZnO/HA at room temperature could be proposed as physical adsorption while the reactions between H_2S and nZVI at high temperatures are probably attributable to both physical and chemical adsorption processes. This difference may have contributed to such different results. However, further investigations are needed to confirm the hypothesis and to optimise the absorbent capacity and energy demand.

Other studies have focused on creating hybrid systems to improve existing technology. Studies showed that loading metal oxide on activated carbon (AC) increased the adsorption capacity of the support (Kim et al., 2012). The preparation of these hybrid materials with NPs of metal oxides could be very promising since nano-sized materials have a higher overall surface area for the adsorption of more gas molecules. Balsamo et al. (2017) prepared a hybrid system by dispersing mixed ZnO and CuO NPs onto a commercial AC at a fixed total metal loading of 10% wt. Functionalised sorbents showed a significantly larger adsorption capacity than raw AC. Azamuddin et al. (2021) studied the effect of several oxide NPs on AC (palm shell AC), finding more efficient results compared to raw AC adsorbent. Among metal oxide NPs, CuO/AC adsorbent gave a higher adsorption capacity (86.60 mg H_2S g^{-1} CuO/AC) at room temperature when synthetic biogas flowed through a fixed-bed adsorption column filled with NPs/AC with an inlet H_2S concentration of 3,000 ppm. Table 2 compares the H_2S removal capacity of the above-mentioned articles.

Table 2: Summary of adsorption capacity at breakthrough point reported in the literature

Nanoparticles or hybrid materials	**System**	**H_2S removal capacity (mg H_2S g NPs^{-1}) at breakthrough point**	**Reaction temperature (°C)**	**H_2S inlet (ppm)**	**References**
CeO/AC	Fixed bed adsorption column	4.03	30	3,000	Azamuddin, et al. (2021)
NiO/AC		9.06			
CuO/AC		86.6			
FeO/AC		11.08			
DT-Fe NPs not thermally treated	Custom-designed fixed-bed reactor	14.72	250	10,000	Li et al. (2020)
DT-Fe NPs thermally treated at 300°C		183.5			
DT-Fe NPs thermally treated at 400°C		408.3			
DT-Fe NPs thermally treated at 400°C		14.4			
Nano zero-valent iron	Custom-designed quartz fixed-bed reactor	12.56	room temperature	10,000	Su et al. (2018)
		14.77	100		
		391.02	200		
		488.95	250		
ZnO (5wt%) /HA	U-shaped Pyrex glass tube	~ 5	30	1,450 (ppmv)	Van-Pham et al. (2022)
ZnO (15wt%) /HA		26.3			
ZnO (30wt%) /HA		~ 11			

Ma and Zou, (2018) investigated the effect of Cu and CuO NPs on the mass transfer of H_2S in the scrubbing process with methyldiethanolamine (MDEA) calculated using a double-contact column tower. The work aimed to increase the mass transfer coefficient thanks to NPs to enhance the desulfurisation effect. Two stable and homogeneous nanofluids were prepared: MDEA-based Cu and MDEA-based CuO at different concentrations (from 0.02 vol% to 0.1 vol%). The addition of such particles in the adsorbent MDEA enhanced the mass transfer coefficient up to 7.75 mmol (s m^2kPa)$^{-1}$ for CuO nanofluids 0.06 vol % at 20°C with 1,000 ppmv of H_2S starting concentration in biogas. This value was higher than MDEA only. Hence, adding NPs can promote gas-liquid mass transfer in desulfurisation, thereby enhancing the process.

In conclusion, the use of NPs for the ex-situ upgrading of biogas can lead both to foster the development of new technologies based on NPs and to improve the existing technologies (AC and chemical scrubbing). However, there is a need to carry out further studies to better understand the mechanisms of action and to allow the setup of more efficient systems economically competing with the current ones, such as the use of activated carbon. Additionally, it would be necessary to focus on life-cycle assessments and technical-economic studies. These approaches are crucial for evaluating not only the environmental impacts but also the economic effectiveness, ensuring a comprehensive understanding.

1.5 Biological treatments using nanoparticles

An innovative alternative solution for biogas upgrading is biological treatment. In this context, the fermentative CO_2 reduction opens new perspectives for a renewable energy source (Kougias et al., 2017). In this process, the raw biogas can be upgraded in an *ex-situ* reactor by converting the biogas CO_2 and H_2 from exogenous sources to valuable compounds (e.g., acetate, ethanol, butyrrate). Many organisms, including homoacetogens and acetogens, can conduct this process. This new technology seems to be the most environmentally and economically beneficial way to upgrade biogas. The cost of H_2 can be a hurdle for a full-scale application of this kind of process (Omar et al., 2018; Zhao et al., 2020), but various types of NPs can be used to enhance the biological H_2 production. Some microorganisms growing on selected carbohydrates and organic wastes are able to generate bio-H_2, and NPs would stimulate this kind of activity. This could potentially mitigate H_2 production costs while concurrently reducing environmental impact (Maroušek, 2022b).

Wu et al. (2023) studied how nZVI affected the biomethane purity and acetate yield and how the microbiome responded to different nZVI concentrations. The results indicated that appropriate concentrations of nZVI in the biogas upgrading microbiome enhanced the fermentative CO_2 reduction process and the acetate recovery. 500 mg L^{-1} of nZVI led to the best results, with a relative content of CH_4 of 94%, a CO_2 utilisation efficiency of 96%, and an acetate yield of 19 mmol L^{-1}, while the blank test showed an acetate yield of around 13.5 mmol L^{-1}. The increased biogas upgrading efficiency was probably related to an increase in extracellular polymeric substances due to nZVI, which ensures the microbial activity and stability of the ex-situ biogas upgrading. However, further studies and investigations will undoubtedly be necessary to determine the feasibility of the treatment and identify the mechanisms of interaction between NPs and microbial activity.

Another innovative solution for biological treatment is the use of microalgae. The microalgal cultures can use CO_2 present in biogas thus reducing its content (Meier et al., 2015). Another advantage of this kind of biotechnology is the possibility of producing significant amounts of biomass for the subsequent generation of biogas or other biofuels and other value-added products, which would significantly improve the energy balance of the biogas plant (Alcántara et al., 2013; Ho et al., 2013).

Vargas-Estrada et al. (2023b) studied the effect of three different iron-based NPs added to *Chlorella sorokiniana* batch cultures, devoted to photosynthetic biogas upgrading to enhance CO_2 biofixation: Fe_2O_3, carbon-coated nZVI-NPs containing 7% (wt%) of Fe (CALPECH NPs) and carbon-coated nZVI-NPs containing 31% (wt%) of Fe (SMALLOPS NPS). All three types of NPs enhanced algal development. In particular, adding 70 mg L^{-1} of CALPECH NPs resulted in a two-fold enhancement in the microalgae productivity and a carbohydrate and lipid content increase by 56% and 25%, respectively, compared to the control assay.

The same authors also studied the effect of 70 mg L^{-1} CALPECH NPs in an indoor pilot-scale algal open pond interconnected to a biogas purification column (Vargas-Estrada et al., 2023a). Adding NPs to the culture broth (*Chlorella sp*. and bacteria) led to more efficient upgrading of the biogas: CO_2 removal increased from 86% to 92%. At the same time, H_2S was completely oxidised to SO_4^{2-} by chemolithotrophic bacteria, using the oxygen produced by the algal photosynthetic activity. This entailed an increase of the CH_4 concentration in the upgraded biomethane from 83% to 91%. Moreover, biomass concentration grew from 1.56 to 3.26 g VSS L^{-1}. The authors explain the CO_2 capture enhancement by the addition of NPs with three potential mechanisms. The first one is the reduction of the gas bubble size due to the presence of NPs. The reason for this phenomenon is the collision between NPs and gas bubbles, leading to an increased surface area of the bubbles and enhancing the mass transfer area (Kim et al., 2008). This phenomenon is referred to as the "Bubble breaking effect." The second mechanism, named the "Shuttle effect," is attributed to the interaction between gas and NPs, leading to the adsorption of gaseous components on the surface of the NPs, thereby facilitating their transport before being gradually released into the aqueous medium. The last one, known as the "Hydrodynamic effect," involves the collision of NPs, inducing turbulence and refreshing the liquid-gas boundary layer. In simpler terms, moving NPs collide and create turbulence, thereby enhancing the exchange between liquid and gas (Choi et al. 2015).

These three effects are likely foundational to the outcomes observed by Esmaeili-Faraj et al. (2019). The study utilized synthesized silica NPs in distilled water (with a nanoparticle mass fraction of 0.1%wt) and exfoliated graphene oxide in distilled water (0.02%wt) to augment the efficiency of bioscrubbing treatments. This latter is a hybrid method where the gaseous compound, either CO_2 or H_2S, is absorbed in a liquid, and subsequently, the microorganisms regenerate the contaminated absorbent in a bioreactor (Shareefdeen and Singh, 2005). The authors used the NPs to intensify H_2S absorption in the first part of the bioscrubbing process. The results of H_2S absorption showed that the efficiency of both NPs in water was significantly higher than in base fluid (only distilled water). The H_2S removal efficiencies were 98%, 97%, and 86% in the bioreactor for the base fluid, silica NPs, and graphene oxide, respectively.

1.6 Conclusions

In conclusion, the use of NPs for biogas upgrading holds significant promise. The integration of NPs into biogas upgrading processes enhances both yield and quality. Specifically, the use of metal and metal oxides not only reduces production time but also improves the quality of biomethane, offering notable environmental and economic advantages. Ex-situ treatments, exploiting NPs for the removal of H_2S, demonstrate efficiency, although further, larger scale research and application are warranted. Biological treatments, such as fermentative CO_2 reduction and microalgal utilization, present innovative alternatives, showcasing improved biomethane purity and increased acetate yield, even though research in these areas is still in the early stages.

The economic feasibility of nanoparticle-enabled biogas upgrading is still a critical aspect for widespread adoption. While advancements are evident, a comprehensive economic analysis is necessary, covering synthesis costs, material losses, and recovery potential. Future research should focus on bridging technological advancements with economic viability.

Unsolved questions, such as scalability, toxicity and environmental impact, warrant further exploration. Life cycle analyses should assess both environmental impacts and economic feasibility. Addressing these aspects will allow to assess whether the buzz around the use of NPs for biogas upgrading is justified.

Declaration of competing interest

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

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