Mini-Review: Nanoparticles for Enhanced Biogas Upgrading

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Abstract

In response to climate change, the development of sustainable bioenergy sources, such as biogas generated through anaerobic digestion, has become imperative. However, in order to use biogas as a versatile and continuous energy supply, the removal of undesirable compounds like carbon dioxide and hydrogen sulfide is essential. This mini-review explores the innovative applications of nanoparticles in biogas upgrading, emphasizing their capacity to enhance biogas quality and methane content. Examining the scientific and technical outcomes of nanoparticle utilization, this review highlights the potential advantages and discusses the challenges that must be addressed for these technologies to reach full fruition. Moreover, it evaluates the incentives and feasibility factors that can promote the widespread adoption of nanoparticle-based biogas upgrading, ultimately contributing to a sustainable and environmentally friendly energy landscape.

Keywords

Biogas upgrading

Nanoparticles

Biomethane

Biogas purification nanoparticles

Hydrogen sulfide removal

Highlights

- Nanoparticles are used for biogas upgrading;
- Nanoparticles in digestor reduce the production of hydrogen sulfide;
- Nanoparticles are tested in ex-situ upgrading to adsorb hydrogen sulfide;
- Nanoparticles enhance the performance of biological processes;
- Green synthesis, reuse/regeneration of nanoparticles will be crucial.

1.1 Introduction

Nowadays, bioenergy development has become crucial to reduce the use of fossil fuels as a response to climate change, environmental aspects, and the evolution of the geopolitical scenario (Andriani et al., 2014). Moreover, the conversion of biomass to energy plays a crucial role in the reuse and valorisation of waste. For these reasons, bioenergy production had, and still has, significant development and incentive worldwide (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).

AD can convert biomass and organic wastes such as sewage sludge, municipal organic waste, and animal farm manure into clean energy, allowing alternative use of these waste products (Bauer et al., 2013).

Biologically, AD is a complex process made up of four main phases: hydrolysis, acidogenesis/fermentation, acetogenesis, and methanation (Weiland, 2010). Different consortia of microorganisms carry out different steps, which stand in syntrophic interrelation to produce biogas (Angelidaki et al., 1993; Demirel and Scherer, 2008). The latter is a complex gas mixture that includes methane (CH_4, 0–75%), carbon dioxide (CO_2, 25-50%), and other trace gases such as hydrogen sulfide (H_2S,0–3%), nitrogen (N_2, 0-10%), hydrogen (H_2, 0-1%) siloxanes (0–0.02%), halogenated hydrocarbons (VOC, < 0.6%), ammonia (NH_3, <1%), oxygen (O_2, 0–1%), and carbon monoxide (CO, <0.6%) (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 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).

Nanotechnology could play an essential role in the removal of contaminants from biogas. 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, iron, 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 investigate the existing applications of nanoparticles in biogas upgrading to provide an overview of the use of NPs, highlighting the obtained results and their possible outcomes, envisaging the level of advancement of the research in this field and the information which is still lacking.

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

A state-of-the-art in biogas upgrading technologies is presented, together with a definition and classification of nanoparticles. This will lead to a better understanding of the possible use of nanoparticles in biogas upgrading.

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 (II) chloride ($FeCl_2$) 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.

Ex-situ methods are instead the most used upgrading methods since they are more effective and easier to apply (Ghimire et al., 2021). They can be classified into two groups according to their working mechanism:

the conventional physicochemical ones, which still dominate the market, and the biological treatments (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 don't 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). 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 methane from exogenous H_2 and CO_2 from biogas (Luo and Angelidaki, 2013). Nevertheless, basic and applied research for optimising biological systems is generally still required (Ghimire et al., 2021).

Physicochemical treatments, instead, are established and commonly used technologies. 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}), activated carbon up to $ 1,500/ton) (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. Figure 1 shows a summary diagram of the most common upgrading technology.

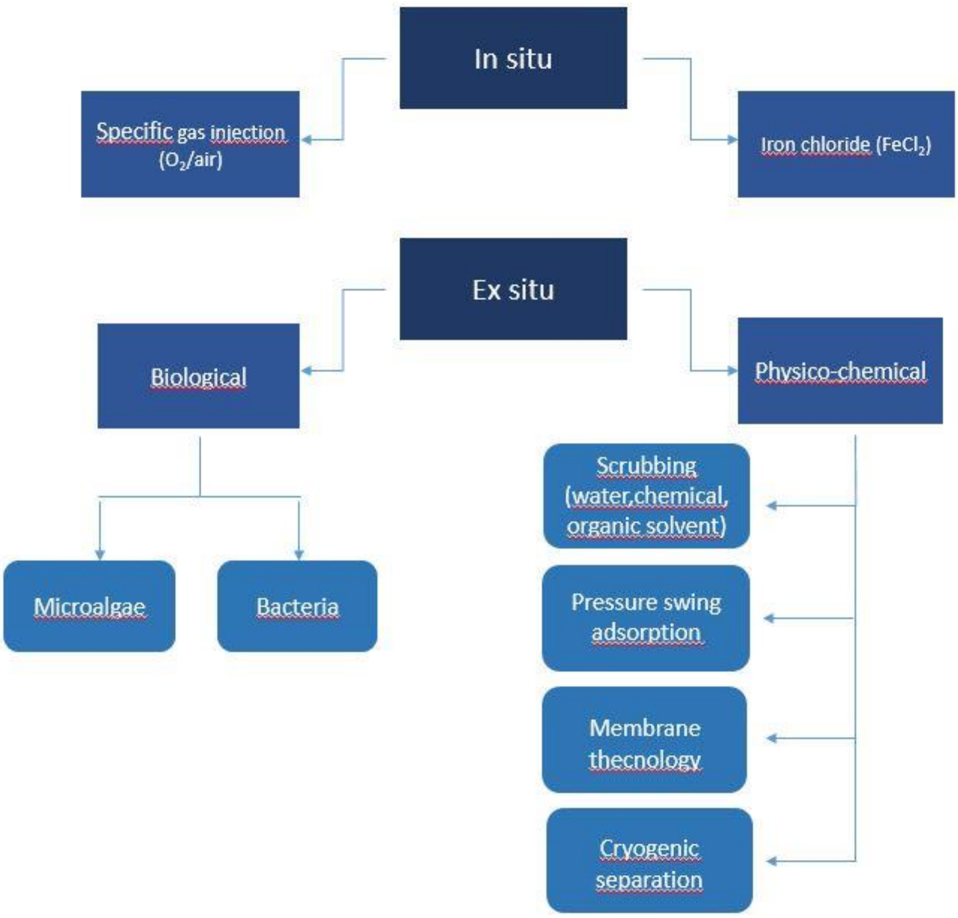

Figure 1: Most common biogas upgrading technologies

Concerning nanoparticles, 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 nanoparticles 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 nanoparticles 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, nanoparticles 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 nanoparticles 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 nanoparticles 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, titanium, and silicon (Sun et al., 2015).

2. Carbon-based nanoparticles: Carbon-based nanomaterials include NPs 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 product 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 Nanoparticles for biogas upgrading

Nanoparticles 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, nanoparticles can be used as adsorbent materials for the creation of new filtering systems, (Su et al., 2012) 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).

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

The addition of nanoparticles 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 nanoparticles 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 silver and titanium, have antibacterial properties that lead to slower microbial growth, reduce biogas yield, and inhibit enzymatic reactions during the AD process. On the other hand, iron, nickel, and cobalt 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 nanoparticles 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 methane production.

As an example, Abdelsalam et al. (2017) analysed the impact of metal nanoparticles (Co, Ni, Fe, and Fe_3O_4) on the biogas production of fresh raw manure. The results obtained in this study showed that using nanoparticles decreased the lag phase, reduced the time to achieve the peak of biogas and methane 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 (ORP) when added into anaerobic systems, creating a more favourable environment for the anaerobic biological process, which requires an ORP between -100 and -300 mV (Jatunarachchi et al., 2006). This leads, for example, to an enhancement in acetate production during acetogenesis, which requires an ORP around -300 MV (Ren et al., 2007), with a consequent increase in the biomethane produced through autotrophic methanation.

Lastly, metal nanoparticles 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 nanoparticles 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 (Abdelwahab et al. 2023 a; 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 nanoparticles used. Su et al. (2012) observed a reduction of the concentration of H_2S in biogas by 98.0 % compared to the control by adding 800 mg L^{-1} in weight (2g in 200g of dewatered biomass) of nanoparticles of zero-valent iron (nZVI). This was attributed to the reducing power of zero-valent iron, 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 anaerobic digestion. 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):

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

Other reports report that high concentrations of nZVI inhibit sulfate-reducing bacteria (SRB), which are responsible for producing hydrogen sulfide 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 SRB activity.

Also, other metallic NPs could inhibit SBR activity, as reported by Liu et al. (2021), who found a decrease in hydrogen sulfide production in the bioreactor at 200 mg L^{-1} Ni NPs due to SRB inhibition. However, these concentrations are high, especially in the case of iron. Hence, the inhibition could happen only when a very high dosage is used.

Gran et al. (2022) studied the effects of 100 mg L^{-1} of NiO, CoO, and Fe_3O_4 nanoparticles 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 18.32%, 13.36%, and 27.75%, 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.

Abdelwahab et al. (2023a) also found a 47.5% H_2S decrease by adding 2 mg L^{-1} Ni nanoparticles 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 (Abdelwahab et al., 2023a).

Many authors also tested different combinations and concentrations of nanoparticles inside the digester to achieve better removal capacities. As an example, Hassanein et al. (2019) found 100% removal of hydrogen sulfide 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 SRB could occur due to high dosage.

However, it could be necessary to consider any toxicity that may be caused by the combination of different nanoparticles, especially at high concentrations, since detailed studies on toxicity are lacking (Rocha-Meneses et al., 2022). Further, nanoparticles in digestate could hinder its possible reuse and valorisation

(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 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 (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	14.16%	30 days at 33±0.5°C	Abdelwahab et al. (2023a)
		2	47.50%		
		4	34.16%		
cattle manure	Fe, Ni, Co	30 Fe, 2 Ni and 1 Co	24.19%	15 days at 33±0.5°C	Abdelwahab et al. (2023b)
		30 Fe, 2 Ni, 0 Co	26.02%		
		30 Fe, 0 Ni, 1 Co	14.47%		
		0 Fe, 2 Ni, 1 Co	2.59%		
cattle manure	Fe	15	45.00%	30 days at 33±0.5°C	Abdelwahab et al. (2022)
		30	48.50%		
		60	52.50%		
cattle manure	Fe_2O_3	100	33.59%	30 days at 38°C	Farghali et al. (2020)
		500	46.30%		
		1000	53.52%		
cattle manure	Fe_2O_3	20	33.03%*-88.29%	30 days at 38°C	Farghali et al. (2019)
		100	35.81%*-96.44%		
	TiO_2	100	35.08%*-97.47%		
		500	35.9%*-98.10%		
	Fe_2O_3 and TiO_2	20 Fe_2O_3 100 TiO_2	41.55%*-98.77%		
		100 Fe_2O_3 500 TiO_2	36.83%*-83.82%		
primary sludge		100 NiO,100 CoO,100 Fe_3O_4	52.57%	35 ± 1 °C	Gran et al. (2022)

and waste activated sludge of WWTP	Ni, CoO, Fe_3O_4 combinated	1 NiO ,1 CoO,100 Fe_3O_4	32.83%		
	Fe_3O_4	100	27.75%		
	NiO	100	18.32%		
	Co	100	13.36%		
poultry litter	Fe, Ni, and Co combinated	1000 Fe, 120 Ni, and 54 Co	100% in first 28 and 34 days after NPs addiction. 56.3% 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	100.00%	79 days, 35°C	Hassanein et al. (2019)
		400 Fe, 48 Ni, and 21.6 Co	71.90%		
		200 Fe, 24 Ni, and 10.8 Co	40.90%		
		100 Fe, 12 Ni, and 5.4 Co	11.90%		
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 methane production by 28%. The authors suggest that iron NPs can undergo an oxidation/reduction reaction with CO_2 and water to produce iron carbonate and hydrogen according to the following reaction:

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

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 carbon dioxide into methane, reducing the amount of CO_2 in the biogas and increasing methane 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 conclude.

1.3.2 Ex-situ: physicochemical treatments using nanoparticles

Nanoparticles 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 nanoparticles 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 iron 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 zero-valent iron and could be as follows:

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

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

Li et al. (2020) obtained similar results and conclusions with iron nanoparticles synthesised 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 a zero-valent iron and water suspension at room temperature. In this case, the use of an aqueous solution with nanoparticles 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 nanoparticles (HA) combined with ZnO at room temperature (ZnO/HA). The results showed a removal capacity of 26.3 mg S g^{-1} with the sorbent ZnO (15 wt%)/HA nanoparticles 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 hydrogen sulfide 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 nanoparticles 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 zinc and copper oxide nanoparticles onto a commercial activated carbon at a fixed total metal loading of 10% wt. Functionalised sorbents showed a significantly larger adsorption capacity than raw activated carbon. Azamuddin et al. (2021) studied the effect of several oxide nanoparticles on activated carbon (palm shell activated carbon), finding more efficient results compared to raw AC adsorbent. Among metal oxide nanoparticles, 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	**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	12.56	room temperature	10,000	Su et al. (2018)

	quartz fixed-bed reactor	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 nanoparticles 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 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 nanoparticles can promote gas-liquid mass transfer in desulfurisation, thereby enhancing the process.

In conclusion, the use of nanoparticles for the ex-situ upgrading of biogas can lead both to the implementation of new technologies based on NPs and to an improvement of existing technologies (AC and chemical scrubbing). However, there is a need to carry out further studies to understand the mechanisms of action better and allow the realisation of more efficient systems capable of economically competing with the systems used nowadays, such as activated carbon.

1.3.3 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 CO_2 and H_2 (exogenous) to valuable compounds (e.g., acetate, ethanol, butyrate). 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 (Omar et al., 2018; Zhao et al., 2020).

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 94.1 %, a CO_2 utilisation efficiency of 95.9 %, and an acetate yield of 19.4 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.

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 nanoparticles added to *Chlorella sorokiniana* batch cultures, devoted to photosynthetic biogas upgrading to enhance CO_2 biofixation: Fe_2O_3, carbon-coated zero-valent iron NPs containing 7.26 % (wt%) of iron (CALPECH NPs) and carbon-coated zero-valent iron NPs containing 31.38% (wt%) of iron (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, Hoyos, Méndez, et al., 2023). Adding NPs to the culture broth (*Chlorella sp*. and bacteria) led to more efficient removal of the pollutant compounds from 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:

1) Bubble breaking effect, where NPs reduce the size of bubbles, thus increasing the diffusion area;

2) Shuttle effect, where the gas is adsorbed to the NPs surface and is then released into the liquid;

3) Hydrodynamic effect, where the NPs collide, inducing turbulence and refreshing the liquid–gas boundary layer (Choi et al. 2015).

Lastly, Esmaeili-Faraj et al. (2019) used synthesised silica NPs in distilled water (with nanoparticle mass fraction of 0.1%wt) and exfoliated graphene oxide in distilled water (0.02%wt) to enhance the efficiency of bioscrubbing treatments. This latter is a hybrid method where the pollutant, 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 of biogas in the absorption showed that the efficiency of both NPs in water was significantly higher than in base fluid (only distilled water). The H_2S removal efficiency of 98%, 97%, and 86% in the bioreactor was obtained for the based fluid, silica nanoparticles, and graphene oxide bioreactor.

1.4 Conclusions

The energy crisis that the world is experiencing makes it necessary to use alternative forms of energy. In this sense, the development and improvement of renewables will be crucial shortly (Mohtasham, 2015). Among these, biogas, produced by anaerobic digestion, can play a fundamental role, allowing flexible and continuous energy production (Röder and Welfle, 2019). However, biogas must undergo a refining process for energy production to eliminate polluting compounds such as CO_2 and H_2S. Nanoparticles have many properties that make them usable in this field. Nowadays, the use of NPs, with a particular interest in metallic NPs (iron, nickel, and cobalt especially), is mainly studied during anaerobic digestion as the addition of nanoparticles to the digester can lead to an increase in biogas production by 8–28% (Rocha-Meneses et al., 2022). Some authors highlight that using metallic NPs during AD also leads to removing H_2S through mechanisms of absorption, precipitation, and inhibition of sulfate-reducing bacteria (Yan et al., 2010; Kaksonen and Puhakka, 2007). H_2S reduction until 100% was achieved using a mixture of Fe, Ni, and Co NPs (>100 mg L^{-1}) (Hassanein et al., 2019) and removals around 50% were obtained with the use of Fe (60 mg L^{-1}) and Ni (2 mg L^{-1}) nanoparticles only (Abdelwahab et al., 2023a; Abdelwahab et al., 2022). This makes the produced biogas more valuable, reducing the need for further treatments. However, it is good to point out some drawbacks. Nanoparticles in digestate could hinder its possible reuse and valorisation (Lee and Lee, 2019). High concentrations of nanoparticles and nanoparticles mixture could induce toxicity phenomena for microorganisms operating in the AD and detailed studies on toxicity are lacking (Rocha-Meneses et al., 2022). Lastly, the references report data obtained at lab-scale, which means that major work is still needed to assess the possibility of scaling up the process.

Future research should focus on these issues to enable a broader vision of the benefits and disadvantages arising from this new methodology.

NPs are also studied in ex-situ upgrading as a solution to adsorb H_2S or to improve existing technology (Das et al., 2022). In these cases, also metallic nanoparticles are the most used, probably because of their high reactivity (Viñes et al., 2014). An adsorption capacity greater than 488.95 mg H_2S g NPs^{-1} was achieved when nano zero-valent iron NPs were used as adsorption material at 250°C (Su et al., 2018). Lower values were obtained when upgrading was carried out at room temperature. However, experiments are still in their early stages, and further studies are necessary to make these new technologies economically competitive and applicable on a larger scale. It is believed that to achieve this goal, the focus will be the production of nanoparticles with lower environmental impact and a synthesis process that avoids the use of chemical agents, as in the case of Li et al. (2020), or leading to the valorisation of waste products such as Van-Pham et al. (2022). This could lead to lower production costs and a strong incentive for using green systems.

Increases in H_2S removal efficiencies were also found when NPs were used to improve the existing technology. (Azamuddin et al. 2021) combined copper oxide nanoparticles with activated carbon and obtained a removal capacity of 86.6 mg H_2S $gCuO/AC^{-1}$, compared to 2.85 mg H_2S gAC^{-1} of the raw activated carbon, indicating the use of hybrid materials as a possible new strategy.

Lastly, regarding biological treatments, metal nanoparticles can enhance the performance of the process, even if too few studies have been conducted to conclude.

It is believed that in the coming years, a crucial point for the success of these technologies will be the development of systems that take advantage of the regeneration/reuse of nanoparticles. Metal nanoparticles, the most studied for biogas upgrading, would play a key role due to their physical and chemical characteristics. This would make these technologies eco-friendlier and more cost-effective, allowing competition with activated carbons and iron oxide adsorbents that today allow very limited regeneration (Abatzoglou and Boivin, 2009; Bandosz, 2002; Coppola and Papurello, 2019).

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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