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Review

Microalgae–Nanoparticle Systems as an Alternative for Biogas Upgrading: A Review

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Abstract: Anaerobic digestion is a well-established technology for the sustainable production of biogas. However, to be used as a substitute for natural gas or as vehicle fuel, it is necessary to remove carbon dioxide (CO_2) and other contaminants from biogas that can compromise the useful life of combustion engines. Upgraded biogas is known as biomethane (>95% methane content). This work reviews the different technologies used for upgrading biogas, emphasizing microalgae–nanoparticle systems, representing a more sustainable and environmentally friendly system. Parameters affecting these systems performance are discussed, and the trends and areas of opportunity for subsequent work are evaluated through a bibliometric analysis.

Keywords: biogas upgrading; biogas utilization; biomethane; CO_2 removal; microalgae; nanoparticles

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1. Introduction

The lack of fossil fuels, climate change and environmental deterioration have driven the search, development and implementation of cleaner technologies for energy production. Biogas produced by the anaerobic digestion of organic solid waste and wastewater provides an alternative for producing clean energy in a profitable and eco-friendly way [1,2]. Biogas has a high calorific value (35–44 kJ/g), similar to diesel, kerosene, and liquefied petroleum gas. Typically, biogas is composed of 50–70% methane (CH_4), 30–50% carbon dioxide (CO_2), 0.005–2% hydrogen sulfide (H_2S), < 2% nitrogen (N_2), < 0.6% carbon monoxide (CO), <1% ammonia (NH_3), 0–1% oxygen (O_2), 5–10% water (H_2O), and traces of other gases such as hydrogen, siloxanes and halogenated compounds. However, for its final use and to meet the quality required by most international legislation, biogas must meet the following requirements: $CH_4 > 95\%$, $CO_2 < 2\%$, $O_2 < 0.3\%$ [3]. In this sense, it is necessary to carry out conditioning to improve biogas to eliminate components that reduce its calorific value (such as CO_2, CO, O_2 and water), as well as components that are corrosive and reduce the useful life of combustion engines and power generators (as is the case of H_2S). The resulting clean and improved biogas is known as biomethane [4,5].

There are already various physicochemical technologies to simultaneously eliminate the CO_2 and H_2S contained in biogas (such as chemical washing with alkaline aqueous solutions); however, the operating costs and environmental impact of these technologies limit their application [3]. In this sense, processes based on microalgae offer a competitive and eco-friendly alternative for the simultaneous removal of CO_2 and H_2S contained in biogas. The upgrading of biogas is based on the simultaneous fixation of CO_2 by the action of photosynthetic microorganisms (microalgae) and the oxidation of H_2S to sulfate

(SO_4^{2-}) by sulfur-oxidizing bacteria using the oxygen produced during photosynthesis [6,7]. Furthermore, the effluents generated in the anaerobic digestion process (digestates) can be used as a source of nutrients (mainly nitrogen and phosphorus) for the growth of microalgal biomass, reducing operating costs and the potential for the eutrophication of the digestates [6,8]. Finally, the microalgae–bacteria biomass can be harvested and valorized to obtain other value-added products, improving the economics of the process [9].

A limitation of upgrading biogas using microalgae–bacteria consortia is the mass transfer of CO_2 from the biogas to the washing liquid phase. In this sense, recent research on microalgae–bacteria systems applied to upgrading biogas has focused on increasing the mass transport of CO_2 from biogas to microalgae cultivation [7,10]. Recent studies have used nanomaterials to overcome this limitation, which presents advantages such as a high surface-to-volume ratio, abundant active sites, high reactivity and a high absorption capacity [11,12]. Recent studies demonstrate that metal and carbon nanoparticles improve gas–liquid CO_2 mass transfer [13–16], which translates into an improvement in the methane content in the biogas. To date, the number of published works has increased almost exponentially (Figure 1), which shows the great interest that biogas upgrading using combined systems of microalgae–bacteria and nanoparticle consortia has aroused in recent years. However, the addition of nanoparticles to a microalgae system is a controversial issue, since nanoparticles could inhibit the growth of the microalgae–bacteria consortium, thus decreasing the photosynthetic upgrading of biogas [17].

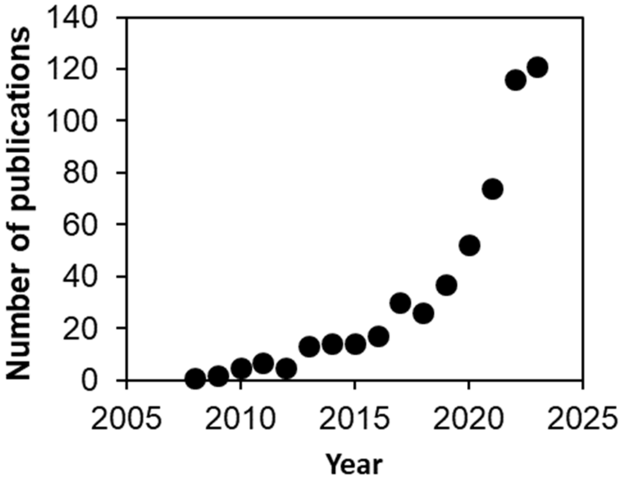

Figure 1. Evolution of the number of publications associated with the upgrading of biogas using microalgal systems with nanoparticles (https://www.sciencedirect.com; accessed on 10 May 2024).

To date, the use of microalgae–bacteria consortia with nanoparticles has focused on producing microalgae biomass and its intracellular constituents. A current review suggests that nanoparticles improve the growth rate of algal biomass (due to the increase in CO_2 fixation and light conversion) and facilitate the harvest of the biomass; it also discusses the inhibitory effect that they may have on the microalgae cultivation [17]. However, the effect that nanoparticles have on the photosynthetic upgrading of biogas has been little addressed and is a topic of great interest. In this sense, the present work discusses the different technologies applied to the upgrading of biogas, emphasizing microalgae–nanoparticle systems and the parameters that affect the efficiency of these systems and must be considered for the scaling of the process.

2. Biogas: Composition, Characteristics and Applications

2.1. Composition and Characteristics

Raw biogas can be obtained from the anaerobic digestion of various substrates: agricultural biomass (by-products, agricultural waste and animal waste), agroindustrial waste (waste from the transformation of the food chain), or the organic fraction of urban solid waste [18–21]. The composition of biogas varies depending on the nature of the substrate and operating conditions (Table 1). The typical heating value of biogas is 22 MJ/m^3 and depends on the concentration of CH_4 (Table 2).

Table 1. Composition of biogas from different substrates subjected to anaerobic digestion [22] (http://www.biogas-renewable-energy.info (accessed on 30 May 2024)).

Component	Agricultural Waste	Landfills	Industrial Waste	Household Waste	Wastewater Treatment Plant Sludge
CH_4 (%)	50–80	50–80	50–70	50–60	60–75
CO_2 (%)	30–50	20–50	30–50	34–38	19–33
H_2S (%)	0.7	0.10	0.8	0.01–0.09	0.10–0.40
H_2 (%)	0–2	0–5	0–2	-	-
N_2 (%)	0–1	0–3	0–1	0–5	0–1
O_2 (%)	0–1	0–1	0–1	0–1	<0.5
CO (%)	0–1	0–1	0–1	-	-
NH_3 (%)	Traces	Traces	Traces	-	-
Siloxanes (%)	Traces	Traces	Traces	-	-
H_2O (%)	Saturation	Saturation	Traces	6 (at 40 °C)	6 (at 40 °C)

Table 2. Typical characteristics of raw biogas [23].

Property	Value
Specific heat capacity	2.165 kJ/kg K
Molar mass	16.04 g/g-mol
Gas constant	0.518 kJ/kg
Normal density	1.2 g/L
Critical density	320 g/L
Relative density (to air)	0.83
Caloric value of biogas	22.6 MJ/m^3
Critical temperature	−2.5 °C
Critical pressure	7.3–8.9 MPa
Flammability limit content in air	6–12% (*v*/*v*)
Ignition temperature	650–750 °C

2.2. Typical Contaminants in Biogas

2.2.1. Carbon Dioxide

Carbon dioxide is a crucial component in biogas; although its presence does not reduce the useful life of combustion engines, it must be eliminated from biogas to increase its calorific value [24,25]. In this sense, most biogas-upgrading technologies described focus on removing this contaminant.

2.2.2. Sulfur Gases

Biogas produced through anaerobic digestion contains many sulfur compounds, such as sulfides, disulfides, and thiols, which must be eliminated before use. H_2S (the main sulfur compound in biogas) is reactive with most metals, and its reactivity increases with concentration, system pressure, water presence, and elevated temperatures. When burned, H_2S can cause emissions of SO_2, SO_3 or H_2SO_4. Combined with humidity, these components are corrosive to combustion engines and their components, reducing their useful life [26–28].

2.2.3. Halogenated Compounds

Halogenated compounds are frequently found in landfill biogas and oxidized during the combustion process, and in the presence of water, they are corrosive, damaging pipes and equipment.

2.2.4. Siloxanes

Siloxanes are a group of silicones that contain Si-O bonds with organic roots. Many siloxanes are used in cosmetics, food and plastic additives, which are eliminated through wastewater or urban solid waste. So, when biogas is obtained through these wastes, siloxanes are incorporated into the gas stream, given their low boiling point [29,30].

When siloxanes are exposed to high temperatures in an engine or boiler, they leave inorganic silicon residues (hard deposits) on the piston and valves, which causes extensive damage due to erosion or blockage, compromising engine performance and its useful life [31–33].

2.2.5. Ammonia

Generally, up to 100 ppm of this contaminant is accepted. Ammonia is very corrosive in the presence of water, and its combustion causes the formation of nitrous oxide (NO_x), which causes environmental problems [34].

2.3. Biogas Applications

Among the different applications of biogas are the following: (1) boilers, for heat generation; (2) reciprocating engines, microturbines or gas turbines, to obtain electricity and heat; (3) fuel cells, to generate electricity; and (4) injection into gas pipelines, for use as vehicle fuel. CO_2, H_2S and water vapor are the primary pollutants of biogas that are important for use in boilers, cogeneration, vehicle engines, and the natural gas network, so they must be removed from biogas before use [2–4].

No international technical standard exists for injecting biogas into the natural gas network. However, the European Union and the United States have adopted recommendations on the minimum quality requirements for biogas before it is injected into the natural gas network (Table 3). However, not all applications require the same quality of biogas (Table 4). So, raw biogas must undergo one or more treatments before its use, based on the requirements for using the biogas.

Table 3. General requirements for pipeline quality biomethane [3,35,36].

Compound	Unit	USA	France	Germany	Sweden	Switzerland	Austria	The Netherlands
CH_4	% (v/v)				95–99	>96		>80
CO_2	% (v/v)	<2	<2	<6		<6	<2	
O_2	% (v/v)	<0.4	<0.01	<3		<0.5	<0.5	<0.5
H_2	% (v/v)		<6	<5			<4 [c]	<12
$CO_2 + O_2 + N_2$	% (v/v)				<5	<5		
Relative humidity						<60%		
Sulfur	ppm		<100 [a] <75 [b]	<30	<23	<30	<5	<45
	g/100 ft^3	1						
Total inert	% (mol)	5						
Siloxanes	ppm	1						

[a] Maximum permitted; [b] Average content; [c] mole percentage.

Table 4. Requirements to remove gaseous components depending on the biogas utilization [37].

Technology	H_2S	CO_2	H_2O	Siloxanes
Boiler	<1000 ppm	No	No	No
Stationary engine	542–1742 ppm	No	No	9–44 ppm
Kitchen stove	<10 ppm	No	No	No
Vehicle fuel	<5 ppm	Recommended	Yes	No
Natural gas grid	<4 ppm	Yes	Yes	Yes

3. Biogas-Upgrading Technologies

Raw biogas must be enriched and purified to reach natural gas standards through physical, chemical, or biological methods. The selection of the technology used will depend on the final use of the biogas, the efficiency of the process, and the associated costs. Established biogas-upgrading technologies are derived from the natural gas purification industry, which is grouped into two broad categories: (1) physicochemical methods (water scrubbing, physical scrubbing, chemical scrubbing, adsorption processes, cryogenic separation and membrane separation) and (2) biological methods (chemoautotrophic or photoautotrophic methods) [37].

3.1. Physicochemical Methods

These technologies are the oldest used in the removal of contaminants from biogas. The most commonly used methods are absorption processes, which take advantage of the difference in solubility of the contaminants present in biogas (CO_2 and H_2S) and CH_4 in different solvents. When water is used, the solubility of CO_2 and H_2S is 26 and 73 times greater than that of CH_4 (at 25 °C) [37,38]. This difference can be further increased if other solvents are used, such as polyethylene glycol ethers, which have an affinity five times greater for CO_2 than water, thus minimizing the amount of solvent required and the size of the equipment. In both absorption processes, the solvent can be regenerated by means of post-treatment [39,40].

Chemical scrubbing involves a chemical reaction between gases and solvent (usually primary, secondary or tertiary amines, sodium hydroxide and sodium carbonate). This method is highly selective and therefore CH_4 losses are minimal; however, solvent regeneration is very energy-intensive [41,42]. On the other hand, adsorption processes are based on the selective separation of biogas components on a solid surface (adsorbent) by means of van der Waals forces. The most commonly used adsorbents are zeolites, activated carbon and silica gel, due to their high porosity and low cost; however, it is necessary to remove H_2S from the biogas beforehand, since it binds irreversibly to the adsorbent [43,44].

The difference in liquefaction temperatures between CO_2 (-78 °C) and CH_4 (-160 °C) makes it possible to upgrade biogas by cryogenic separation. H_2S and siloxanes can also be separated by this method; however, their corrosive nature makes it necessary to remove them first. The main advantage of this technology is that it does not require the addition of chemicals, and CO_2 is obtained as a commercial by-product; however, high costs limit its application on a large scale [3,5,45].

Membrane separation is based on the selective permeability of membranes (inorganic, polymeric or mixed), which retain CH_4 while allowing the passage of CO_2, water vapor or H_2 through the membrane. This technology is attractive because it does not require the addition of chemicals and has high efficiency and a compact design; however, the high costs of the membrane and its degradation over time compromise its application on a large scale [46,47].

Physicochemical methods are generally low in cost, but post-processing is required to recover contaminants or regenerate sorbents. Table 5 presents a comparative analysis of physicochemical methods. A more detailed discussion of these methods is beyond the scope of this paper; however, there are exceptional works on this subject, such as the reviews by Khan et al. [37], Ahmed et al. [48], Sahota et al. [49], Muñoz et al. [3] and Gkotsis et al. [38], to mention a few.

3.2. Biological Methods

Biological biogas-upgrading technologies can be classified as chemotrophic and photoautotrophic (photosynthetic). The main advantage of these methods is that they allow the conversion of CO_2 into an energy vector (CH_4) under mild reaction conditions (atmospheric pressure and moderate temperature).

Table 5. Comparative analysis of physicochemical technologies applied to biogas upgrading [37,48,49].

Parameter	**Water Scrubbing**	**Physical Scrubbing**	**Chemical Scrubbing**	**Pressure Swing Adsorption**	**Cryogenic Separation**	**Membrane Separation**
Basis of operation	Physical absorption	Physical absorption	Chemical absorption	Adsorption	Multistage compression and condensation	Permeation
Absorbent/adsorbent	Water	Organic solvents, polyethylene glycol	Amines, Alkali solutions	Molecular sieves	No requirement	Polymeric membrane
CH_4 recovery (%)	>97	>99	99.5	>96	97–98	96–98
CH_4 losses (%)	<2	<2	<0.1%	<3,	<2	<1.5
Desulfurization requirement	No	No	Yes	Yes	No	Yes
H_2S co-removal	Yes	Possible	Contaminant	Possible	Yes	Possible
Energy consumption (kWh/Nm^3)	0.46	0.49–0.67	0.27	0.46	0.18–0.25	0.25–0.43
Cost investment (EUR)	265,000	1,000,000	353,000	680,000	-	233,000
Cost maintenance (EUR)	15,000	39,000	59,000	56,000	-	25,000
Advantages	- Simple process. - No pre-cleaning required. - No chemical required. - Easy water regeneration - Simultaneous removal of H_2S and NH_3.	- High methane purity. - Less methane loss. - Regenerative. - No corrosion problems. - Simultaneous removal of H_2S, H_2O and NH_3.	- Higher efficiency. - Less methane loss. - Faster process. - Complete H_2S removal. - High CO_2 removal.	- Dry process. - No chemical usage. - No water demand. - Adsorption of N_2 and O_2. - Compact process. - Flexible.	- Highest methane purity. - No chemicals required. - High methane purity. - Lower energy cost. - Easy scaling-up.	- Dry process. - No chemicals. - Simple and compact process. - Low energy consumption. - Good selectivity. - Scale-up flexibility. - No hazardous emissions.
Disadvantages	- Higher water requirement. - Lower efficiency. - Slow process. - Corrosion problem. - Wastewater disposal.	- Solvent is expensive. - Expensive due to higher maintenance cost. - Solvent is expensive.	- Use of chemicals. - Higher investment cost. - Solvent is toxic for humans and environment. - Biogas desulfurization is required.	- Desulfurization is required. - Expensive process. - High methane losses.	- High capital and operating cost. - Huge amount of energy required. - Efficiency of the process is temperature-dependent.	- Pre-treatment required. - Membranes are expensive. - High energy demand. - Degradation of membranes with time.

3.2.1. Chemolithotrophy

This method is based on the conversion of CO_2 to CH_4 by the action of CO_2-reducing methanogenic archaea (hydrogenotrophic methanogenesis), according to the following chemical reaction:

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O \quad (\Delta G = -130.7\ kJ/mol) \qquad (1)$$

Methanogenic archaea that are frequently reported in anaerobic digesters for the conversion of CO_2 to CH_4 belong to the genera *Methanobacterium*, *Methanospirillum*, *Methanothermobacter*, *Methanobrevibacter*, and *Methanococcus* [50]. Previous studies have shown that a continuous supply of H_2 to the system results in improved biogas with at least 95% CH_4. However, this technology is limited by the poor gas–liquid mass transfer of anaerobic digester [48,50]. It is important to stress that to make this technology techno-economically attractive, the H_2 must come from a renewable source, such as the electrolysis of water using excess electricity, where H_2 is produced as a by-product [51], or from residual electricity from windmills or solar panels [4]. This process can occur under in situ, ex situ, and hybrid configurations.

3.2.2. Photoautotrophy

Photosynthetic biogas upgrading takes advantage of the ability of microalgae to capture CO_2 and obtain a gas rich in CH_4. This process is carried out by photoautotrophic microorganisms such as prokaryotic algae (cyanobacteria) or eukaryotes (green algae), which fix CO_2 in the presence of light [4,52]. Typically, microalgae coexist with bacterial cultures, which oxidize H_2S (using the O_2 supplied by the microalgae), allowing for the simultaneous removal of CO_2 and H_2S, with CH_4 contents up to 97% in the upgraded biomethane [53].

Approximately 1.8 g of CO_2 is necessary to produce 1 g of microalgae. However, CO_2 concentrations > 5% can inhibit the growth of microalgae. This way, high-CO_2-tolerant microalgae species are necessary for upgrading biogas [54]. This technology can be carried out in both closed (tubular) and open photoreactors (high-rate algal ponds (HRAPs) or raceways). Closed reactors are more efficient in biogas upgrading and require less space and water; however, energy requirements are a limitation for real-scale processes.

On the other hand, open reactors have a lower energy demand and lower construction and operation costs [4,55]. The raw biogas is injected directly into the photobioreactor or a column external to the main tank. In this way, microalgae, in the presence of light and nutrients, fix CO_2 and produce biomass, oxygen, and heat. A biomethane that complies with international regulations and biomass that can be used commercially to obtain value-added products (biodiesel and pigments, among others) are obtained [56–59]. The microalgae species most frequently used in the biogas-upgrading process include the genera *Chlorella*, *Arhtrospira*, and *Spirulina* [3], since they tolerate high concentrations of CO_2 and pH (Table 6). However, using axenic cultures is a limitation for practical applications, and the use of microalgae–bacteria consortia (sulfur-oxidizing) implies a simultaneous removal of CO_2 and H_2S, preventing high O_2 content in the biogas and minimizing the toxic effect of H_2S on microalgae [4,60]. In this sense, it is necessary to establish the design and operating conditions (type of reactor, type of light, hydraulic retention times, etc.) that allow for the long-term stability of the process.

Table 6. Photosynthetic biogas upgrading using microalgae.

System	Species	CO_2 Removal (%)	CH_4 (%)	Ref.
HRAP	*Chlorella vulgaris*	80		[61]
Closed photobioreactor–bags	*Chlorella vulgaris*	43.21–55.39	76.21–80.40	[62]
	Scenedesmus obliquus	49.95–62.31	78.53–82.79	
	Neochloris oleoabundans	40.25–54.39	75.19–80.06	
Open photobioreactor	*Nannochloropsis gaditana*	81		[60]
Closed photobioreactor	*Scenedesmus* spp.	66.7	64.7 ± 6.9	[63]
HRAP	*Mychonastes homosphaera*	98.8	96.2	[64]
HRAP	*Geitlerinema* sp. (61.5%), *Staurosira* sp. (1.5%) and *Stigeoclonium tenue* (37%)	98.8	97.2	[53]
HRAP	*Chlorella* sp.	95	94	[7]

4. Hybrid Systems (of Microalgae and Nanoparticles) in Biogas Upgrading

4.1. Nanoparticles in Biogas Upgrading

Nanotechnology is increasingly focusing on ecologically sustainable development in environmental sciences. Nanotechnology also offers ways to obtain biofuels such as biodiesel, bioethanol and biogas.

Nanoparticles (NPs) have offered new environmental and engineering opportunities, such as increasing biogas production and removing contaminants from wastewater. NPs have a favorable impact that increases the rate of CH_4 production, along with the stability of the anaerobic digestion process [65].

Recently, magnetite has been successfully used to improve biogas production. However, other materials, such as ZnO, CuO, Mn_2O_3, and Al_2O_3 [66], have shown the opposite effect when used as additives during anaerobic digestion. In this context, an adequate evaluation of the physicochemical characteristics of NPs and operational conditions, such as substrate type, particle size, temperature, pH, carbon/nitrogen ratio (C/N), concentration of volatile fatty acids (VFA), total alkalinity (TA), degradation of total solids (TS) and volatile solids (SV) and the concentration of the inoculum, are mandatory [67]. The NPs that have shown better performance during anaerobic digestion are granular activated carbon (GAC) and metal-based NPs, more specifically iron oxide nanoparticles (IONPs) in three forms Zero-Valent Iron (Fe^0), hematite (Fe_2O_3) and magnetite (Fe_3O_4). The authors report that applying Fe^0 results in better CH_4 yield [68,69] mainly because of their magnetic properties and strong chemical stability, significantly improving electron transfer during anaerobic digestion. In this way, interspecies electron flow is achieved by directly transmitting electrons produced by electron-donating bacteria (EDB) to acceptors. Thus, methanogenic archaea convert CO_2 to CH_4 using the electrons supplied from the EDB through conductive materials. Iron oxides function as electron-conducting nanowires and accelerate their flow between species without mediating molecules, such as hydrogen or formate [69].

In previous studies where iron NPs were used, the production of CH_4 was demonstrated by the release of two electrons as a result of Fe^0 oxidation to Fe^{+2} under anaerobic conditions. In this way, inorganic CO_2 can uptake these electrons, accelerating the hydrogenation process and production of CH_4. Furthermore, these NPs act as catalysts for the dehydrogenation of formic acid, obtaining CO_2 and H_2 as products, which react to generate more CH_4 [70]. Nickel (Ni) is used by bacteria for the anaerobic digestion process, making it essential for methanogenic archaea and acidogenic bacteria. Nickel (Ni) potentially forms soluble organic complexes with specific amino acids [71]. Cobalt (Co) is an important trace element for the growth of methanogenic archaea during digestion. Cobalt is necessary for methanogenic archaea that break down methanol. Indeed, Co is considered a key component in the oxidation of acetate to CO_2 and H_2, leading to the hydrogenotrophic methanogenic process [72].

The optimal concentrations of Fe (5, 10, 15 mg/L), Ni (1–4 mg/L), and Co (1 mg/L) NPs for treating livestock manure and improving both the production and quality of biogas are shown in Table 7. However, more studies are required on mixtures of NPs (and their interactions) or other substrates other than livestock manure for biogas production. Moreover, it is widely known that methane yield depends on the type of substrate and is limited by the hydrolysis step. Thus, using NPs as additives to improve the hydrolysis rate in the anaerobic digestion process has been encouraged [73]. In other words, adding NP mixtures can increase the effectiveness of CH_4 production. For instance, NPs that have beneficial effects on the anaerobic digestion process, i.e., Fe, Ni and Co NPs, could be combined to improve the methane yield in substrates such as cattle manure [65]. For instance, the electrons released by Fe^0 can be consumed by inorganic CO_2 and thus increase the yield of CH_4. At the same time, Ni (nickel) is a constituent of the cofactor F430, which is the prosthetic group of the methyl coenzyme M reductase complex. This enzyme catalyzes the last step of the CH_4 formation pathway. Co is also a cofactor of methyltransferases and carbon monoxide dehydrogenase (CODH)—the latter is a key enzyme for both the production and consumption of acetate and is present in both acetogenic bacteria and methanogens [65]. In this way, metal NPs and metal oxides are suitable materials to improve the methane content in biogas. However, special attention is required since they can inhibit the process (decreasing methane yield or productivity) if not used in optimal doses [74].

Table 7. Use of NPs in biogas production to improve methane content.

NPs	Size (nm)	NPs Concentration	Substrate	HRT (Days)	Temperature (°C)	Observations	Ref.
Co Ni		1 mg/L 2 mg/L	Cattle manure	50	37	NPs significantly increased the biogas volume ($p < 0.05$) by 1.64 and 1.74 times	[75]
Fe_3O_4	20–40	100 mg/L	Cattle manure	30	38	19.74% increase in methane yield.	[76]
Fe	435.1	15–60 mg/L	Cattle manure	30	37	Increase in specific methane production (118.8%) with 30 mg/L of NPs. Additionally, it decreased the H_2S production rate by 93%.	[77]
Ni	30–80	12 mg/L	Poultry litter	69	-	The addition of Ni increased methane production by 38.4%.	[78]
Ni	65–114	1–4 mg/L	Cattle manure	30	37	The methane yield increased (70.46%) and the H_2S production decreased up to 90.47%.	[79]
Co	-	200 mg/g-SST	Synthetic wastewater	12	35	CH_4 production decreased.	[80]
Co	70–104	1–3 mg/L	Cattle manure	30	37	It improved the hydrolysis rate from 66.66 to 144%.	[79]
Fe_2O_3 TiO_2	25	100 mg/L + 500 mg/L	Cattle manure	30	38	Biogas and CH_4 production were 1.13 and 1.15 times higher than control. H_2S reduction by 62%.	[81]
Fe Ni Co		200 mg/L Fe + 24 mg/L Ni + 10.8 mg/L Co	Poultry litter	79	37	Increases specific methane production by 8.6%.	[78]
Fe Ni Co	103–116 65–114 70–104	30 mg/L + 2 mg/L + 1 mg/L	Cattle manure	15	37	NPs increased CH_4 production by 19.30%. H_2S production decreased by 35.10%	[65]

4.2. Microalgae–Nanoparticle Systems in Biogas Upgrading

Biological methods for biogas upgrading based on photosynthetic microorganisms, i.e., microalgae are considered a cost-effective technology since they do not require intense energy and/or chemicals. Additionally, using microalgae to upgrade biogas can pave the way to a photobiorefinery concept if centrate is used as a culture media and the produced microalgal biomass is used for producing high-added-value products.

Biogas upgrading via microalgae cultures is a technology that has been widely studied at the laboratory and pilot scales [82,83] in systems composed of open high-rate algal ponds (HRAPs) interconnected, employing a settler, with a purification column (PC), where the biogas is sparged to be upgraded to biomethane. The microalgal broth from the PC is returned to the HRAP, and the biomass from the settler is recirculated to the HRAP to prevent its fermentation (Figure 2). This specific system setting has demonstrated high robustness, and CO_2 removals of up to 99% have been reached [8,84]. It is important to highlight that these high CO_2 removals have been recorded under high-alkalinity environments where typically the IC concentration ranges between 1000 and 2000 mg/L and the pH is >9 (Table 8). Indeed, the quality of the upgraded biomethane is governed by environmental parameters, such as the IC concentration, pH, and L/G ratio.

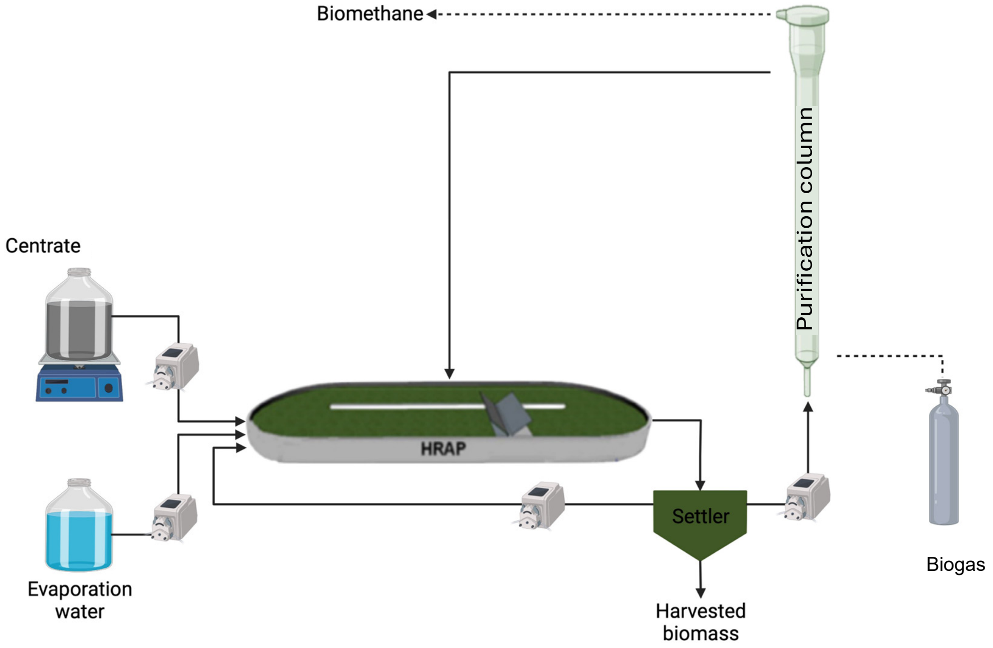

Figure 2. Schematic representation of the photosynthetic biogas-upgrading system.

Table 8. Influence of IC concentration, pH and L/G ratio on the CO_2 and H_2S removals, biomass concentration and biomass productivity. Note: rows marked in gray refer to outdoor conditions.

HRAP Volume (L)	IC (mg/L)	pH HRAP	L/G Ratio in PC	CO_2 Removal (%)	H_2S Removal (%)	Biomass Concentration (g/L)	Biomass Productivity ($g/m^2/d$)	Ref.
180	1500	10.2	1	99	-	2.6	15	[64]
180	1500	8.4–9.6	0.5	94	99	NA	NA	[85]
	500		0.5	94	96	NA	NA	
	100		0.5	92	93	NA	NA	
180	1500	NA	0.5	97–98	99–100	NA	14	[86]
9.2	NA	9.5	9	74	99	1.4	22.8	[87]
	NA	9.6	9	60	80	1.1	18.6	
	NA	9.4	9	42	79	1.3	24.1	
25	1200	9.5	5	89	-	1.23	-	[84,88]
	1000	9.7–9.4	5	94	-	0.23	-	
180	1500	11	0.5	99	99	0.43	7.5	[84]
	1500	10.5	0.5	98	99	0.54	7.5	
	500	10.5	0.5	73	99	0.44	7.5	
	500	9.7	0.5	75	99	0.45	7.5	
	100	7.2	0.5	67	99	0.2	5–7	
	100	7.5	0.5	71	99	0.18	5–7	
180	1430	10.6	0.5	99		1.21	15	[8]
	1430	10.1	0.5	97		0.82	15	
	1430	10.6	0.5	99	-	0.67	8.3	
180	1200	9.7	0.5	93–97	-	0.8	15	[89]
	2400	9.8	0.5	98–99	-	0.4	15	
	2400	9.7	0.5	98–99	-	1.38	0	

Table 8. *Cont.*

HRAP Volume (L)	IC (mg/L)	pH HRAP	L/G Ratio in PC	CO_2 Removal (%)	H_2S Removal (%)	Biomass Concentration (g/L)	Biomass Productivity (g/m^2/d)	Ref.
180	500	8.3	0.5	65–87	-	0.66	15	
	2000	9.9	0.5	87–92	-	1.07	15	
	2000	9.4	1	95–97	-	0.66	15	
	2000	9.6	2	95–97	-	0.66	15	
	2000	9.8	5	95–97	-	0.66	15	
180	1663	9.2–9.4	1	83–96	-	0.31–0.05	0	
	2238	9.3–9.6	1	89–98	-	0.58	7.5	
	2779	9.4–9.5	1	97–98	-	0.51–0.57	15	
	NA	9.6–9.8	1	97–99	-	0.51–0.62	22.5	
	4138	9.6	1	97–98	-	0.42	15	
180	1200	9.1	0.5	95	-	NA	NA	
	1200	9.1	1	95	-	NA	NA	
	1200	9.1	2	98	-	NA	NA	
96,000	500	7.3	1.2	75	91–96	0.33	NA	
			2.1	84–85	95–98		NA	
			3.5	91	99		NA	
	500	7.1	1.2	78–81	99	0.37	NA	
			2.1	87–90	99		NA	
			3.5	94	-		NA	
	500	8.9	1.2	97–98	98–99	0.56	NA	
			2.1	97–98	-		NA	
			3.5	99	-		NA	
96,000	1907	9.5	1.3	96	-	NA	30	
	1900	9.3	1.7	93	-	NA	30	
	1900	9.2	2.1	86	-	NA	30	
	1900	9	2.4	82	-	NA	30	
180	1332	9.1	1	93–97	-	0.14–0.53	0	
	1332	9.1	1	91–96	-	0.3	7.5	
	1639	9.9	1	97–99	-	0.83	7.5	
	1952	9.9	1	99	-	1.34	15	
	2236	9.8	1	99	-	1.25	15	
180	1600	9–8.3	2	93	-	1.39	22.5	
	600	7.1	2	90	-	1.58	22.5	
	1000	9.3–8.7	2	96	-	1.8	22.5	
	1000	9.2	2	97	-	1.13	22.5	
180	672	8.6	2	76–80	-	0.55–0.68	22.5	
	658	8.9	2	80	-	0.60–0.48	22.5	
	521	8.4	5	91	-	0.39–0.49	22.5	
	1500	9.6	2	93–99	-	0.53	15	
	2100	9.5	2	90–99	-	0.31	0	

For instance, Rodero et al. [84] demonstrated that the IC concentration significantly influenced the CO_2 removal from biogas. As the IC concentration increased from 100 to 1500 mg/L, CO_2 removal increased from 72% to 99% in an indoor system configuration. Similar results were reported by Posadas et al. [7] in a similar experimental setting under outdoor conditions. The authors reported that when the IC concentration was 500 mg/L, CO_2 removals ranging from 65 to 87% were recorded, while when the IC concentration was increased to 2000 mg/L, CO_2 removals ranging from 87 to 97% were reached. In this context, it can be stated that high-alkalinity and -pH environments are mandatory for successful CO_2 gas–liquid transfer in the photosynthetic biogas-upgrading process. In this sense, the CO_2 transfer is governed by Equations (2)–(4):

$$CO_2 + H_2O + CO_3^{2-} \rightarrow 2HCO_3^- \tag{2}$$

$$HCO_3^- \rightarrow CO_2 + OH^- \tag{3}$$

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O \tag{4}$$

On the other hand, photosynthetic biogas-upgrading technology has also been demonstrated to remove H_2S efficiently by two pathways—(1) via the symbiosis created by the microalgae–bacteria consortium, where the O_2 produced by microalgae is used by oxidizing bacteria to oxidize H_2S to ${SO_4}^{2-}$ [94], and (2) via chemical oxidation by the O_2 produced by microalgae (when bacteria is not present)—and is governed by Equations (5) and (6):

$$H_2S + 0.5O_2 \rightarrow S + H_2O \tag{5}$$

$$H_2S + 2O_2 \rightarrow SO_4^{2-} + 2H^+ \tag{6}$$

Even if photosynthetic biogas upgrading has been demonstrated to be a promising technology, the process still presents some drawbacks that need to be overcome before taking this platform to an industrial scale. For instance, the limited CO_2 mass transfer to the liquid broth, the high-alkalinity environments, the L/G ratio, and the limited photosynthetic activity of microalgae have been listed as the most relevant parameters that governed the quality of the upgraded biomethane. Adding carbonate/bicarbonate salts has become a simple strategy to reach IC concentrations between 1000 and 1500 mg/L. However, a significantly higher IC concentration does not necessarily mean a higher biomass concentration. For instance, Franco-Morgado et al. [8] and Marín et al. [10,93] reported biomass concentrations < 1 g/L when the IC concentration in the culture broth was ≤1500 mg/L. Interestingly, Marín et al. [93] reported that when the IC concentration of the system increased from 1500 to 2100 mg/L, the biomass concentration decreased from 0.53 to 0.31 g/L. Thus, it could be stated that IC concentrations > 1500 mg/L entailed CO_2 removals > 90%, but the biomass concentration could be decreased or limited. In this sense, special attention is required to enhance the photosynthetic activity of microalgae to improve the biomass concentration before up-scaling the process.

Recently, nanoparticles (NPs) have caught the attention of researchers of microalgae cultures since it has been demonstrated that some metal-oxide NPs can boost the metabolism of some microalgae strains [17]. Even if the interaction mechanisms between NPs and microalgae are not yet well understood, they are believed to interact indirectly or directly with microalgae. Indirectly, NPs can act as CO_2 adsorbents, enhancing the gas–liquid mass transfer and resulting in the improved CO_2 fixation by microalgae. Studies have demonstrated that adding Fe_2O_3 NPs to the surface of polymeric nanofibers significantly improved the CO_2 fixation and microalgae metabolism of *Chlorella fusca* LEB 111 [13,16,95]. Moreover, SiO_2 NPs have also been demonstrated to enhance the gas–liquid mass transfer of CO_2 to microalgae broths. Interestingly, SiO_2 and SiO_2-CH_3 NPs increased the volumetric mass transfer coefficient by 31 and 145% when they were added to *C. vulgaris* cultures. Additionally, the biomass and fatty acid productivity were boosted. On the other hand, NPs can directly interact with microalgae since they can permeate to microalgae cells and interfere with metabolic pathways. In this way, NPs composed of essential ions, such as Fe^{3+}, Mg^{2+}, Ca^{2+}, and Cu^{2+}, could benefit microalgae metabolism [17]. Fe NPs have been reported to have beneficial effects on microalgae cultures. For instance, Fe_2O_3 NPs enhanced the biomass concentration and the lipid production of *Scenedesmus obliquus* when concentrations < 20 mg/L were added to the cultures [96]. Similarly, Rana et al. [97] observed that adding 20 mg/L Fe_2O_3 to *Chlorella pyrenoidosa* cultures increased the biomass and lipid concentration to 34 and 17%, respectively. On the other hand, adding Fe_2O_3 at 50 and 100 mg/L has been reported to increase the lipid content to 40 and 25% in *C.*

vulgaris cultures, respectively [98]. The addition of $MgSO_4$ NPs resulted in similar findings. Sarma et al. [99] reported that adding 1 g/L of $MgSO_4$ NPs to *C. vulgaris* cultures increased lipid production by 118%. Therefore, adding NPs to microalgae cultures is a promising technique to increase the value of microalgal biomass, which could significantly enhance the cost-effectiveness of the photosynthetic biogas-upgrading process.

In this context, the addition of NPs to microalgae cultures intended for biogas-upgrading processes was recently investigated. First, Vargas-Estrada et al. [100] studied the effect of iron-based mesoporous NPs on *C. sorokiniana* cultures. Three iron-based NPs were used: Fe_2O_3 and carbon-coated zero-valent iron NPs with different physicochemical properties at different concentrations, under visible light and UV + visible light. The authors concluded that the porosity and pore size of the NPs affected CO_2 availability in *C. sorokiniana* cultures differently, and that NPs with higher porosity increased CO_2 availability in *C. sorokiniana*. Thus, the carbon-coated zero-valent iron NPs, better known as CALPECH NPs, increased biomass productivity when added at a concentration of 70 mg/L. The boosting effect of the CALPECH NPs was also confirmed in a mixed microalgae–bacteria consortium [101]. The authors studied the effect of different NPs—SiO_2, Fe_2O_3 and CALPECH NPs—at different concentrations under different light sources (visible and visible + UV). The addition of 70 mg/L CALPECH NPs significantly increased the biomass concentration and carbohydrate production of the mixed consortium. Subsequently, the effect of CALPECH NPs was validated in a 180 L laboratory-scale continuous system for biogas upgrading [100]. CALPECH NPs were added at a concentration of 70 mg/L and added daily to the centrate to maintain the concentration in the system. After adding the CALEPCH NPs, the authors reported an increase in biomass concentration in the HRAP from 1.56 to 3.26 g VSS/L. This intense microalgal activity increased CO_2 removal with a CO_2 concentration of 3.2% in the upgraded biomethane. It is important to highlight that the IC concentration of the system was around 600 mg/L, and the intense microalgal activity reduced the buffering capacity of the system, resulting in a concentration of 437 mg IC/L, which caused the CO_2 removal performance of the system. In this context, Hoyos et al. [102] studied the effect of CALPECH NPs in a similar configuration. The authors tested higher concentrations of 70, 140 and 280 mg/L of NPs and found that 140 mg/L was the optimal concentration to improve system performance. The authors reported an increase in the biomass concentration, and to prevent biomass buildup, biomass productivity was increased from 22.5 to 48.2 g $m^{-2}d^{-1}$. In addition, 95% CO_2 removal was observed when 140 mg/L of the CALPECH NPs was added. It is important to highlight that to prevent the loss of buffering capacity, the authors added 1.7 g/L of Na_2CO_3 to the system and maintained a pH between 9.0 and 9.53. Finally, a subsequent study evaluated the effect of adding liquid CALPECH NPs to a similarly configured system [103]. In this case, it was reported that the addition of liquid NPs significantly increased the pH from 8.6 to 9.3, which mediated an increased buffering capacity that enhanced CO_2 mass transfer into the liquid broth, resulting in an increased biomass concentration from 1.2 to 3.5 g/L. Furthermore, the addition of liquid NPs significantly increased the IC concentration in the HRAP, from 22 mg/L to 700 mg/L. This significant increase in IC concentration in the HRAP mediated a CO_2 removal of 94.2%, resulting in an upgraded biomethane with a concentration of 2.2% CO_2.

In this context, adding NPs to microalgae cultures devoted to biogas upgrading is a promising technique to improve the quality of the upgraded biomethane and the biomass productivity of the systems. The significantly increased biomass productivity could enhance the techno-economic feasibility of the process by producing high-added-value products or biofuels. Thus, even if this approach still needs more research to optimize the process, the results obtained so far suggest that the produced biomass could be valorized to create a photobiorefinery concept, which will pave the way to a circular economy.

5. Factors Affecting Biogas Upgrading in Microalgae–Nanoparticle Systems

5.1. Selection of the Microalgal Species

Microalgae species that grow under mixotrophy conditions offer an advantage, especially when biogas upgrading is coupled with wastewater or digestate treatment. Some aptitudes to consider for the selection of the microalgae species are high growth rates, high cell productivity, resistance to polluting agents and fluctuations in the environment, high tolerance to CO_2, H_2S and mixotrophic metabolism (to maintain cell density even in the dark phase), and accumulating lipids and other value-added products [55,59]. Unfortunately, few species of microalgae meet these requirements, so most of those reported in the literature correspond to the genera *Chlorella* and *Scenedesmus*. It has been described that *S. obliquus* has a higher cell productivity, specific growth rate, CO_2 fixation rate, and cell density than *C. vulgaris* and *C. kessleri*, both in real and synthetic wastewater. On the other hand, microalgae–bacteria consortia present certain advantages since the bacteria can oxidize the H_2S contained in the biogas, avoiding the toxic effects of this component on the microalgae (and decreasing the O_2 content in the upgraded biogas), so wastewater treatment and biogas upgrading are carried out simultaneously [104]. Recently, it has been reported that the microalgae *C. vulgaris* can carry out wastewater treatment (COD and nutrient removal) in a continuous system, both in the light and dark phases (16 h day/8 h night), manipulating the dilution rate. The authors conclude that continuous wastewater treatment for 24 h is possible by applying the recycling and storage of carbohydrate-rich biomass, producing valuable protein-rich biomass at the end of the dark phase [105].

5.1.1. CO_2 Tolerance

CO_2 is the second major component in biogas, generally ranging between 20 and 55% (*v*/*v*) [2–4]. In this sense, a species of microalgae with a high tolerance to CO_2 is desirable. Due to the limited contact time, the microalgae's tolerance to high CO_2 concentrations constitutes a limiting factor. It has been reported that the cyanobacteria *Spirulina*, *Anabaena*, and *Synechococcus* tolerate atmospheres with up to 100% CO_2 without pH control [106,107]. Similarly, it has been reported that *Chlorella* species tolerate CO_2 in a typical range of 40–70% CO_2 [108–110], while *S. ubliquus* tolerates up to 80% CO_2 [111]. Various studies show that increasing the concentration of CO_2 in biogas increases the accumulation of lipids and polyunsaturated fatty acids [112], which implies a more promising biomass for obtaining biofuels at a later stage, promoting the process economy.

5.1.2. H_2S Tolerance

Another important contaminant in raw biogas is H_2S, typically present in 0 to 10,000 ppm concentrations, depending on the substrate and inoculum used. H_2S is acidic in nature, facilitating its elimination using an alkaline solution, similar to the case of CO_2. At the typical pH that microalgae systems operate (between 7 and 9), and in the presence of oxygen (a product of photosynthetic activity), sulfate is quickly produced, which precipitates, even in the absence of sulfur-oxidizing bacteria [113]. This also avoids the toxic effect of H_2S on microalgae growth [113,114].

According to Equation (7), sulfate precipitation will also remove a fraction of oxygen. In this sense, the fraction of H_2S in raw biogas plays an important role in the quality of biogas regarding oxygen content [6]. Different microalgae have been used for biogas desulfurization, and it was found that *C. vulgaris*, *C. sorokiniana*, and a consortium dominated by *Scenedesmus* sp. tolerated concentrations of 200, 3500 and 3000 ppm of H_2S [6,113,115].

$$H_2S^- + 2O_2 \rightarrow 2H^+ + SO_4^{2-} \tag{7}$$

Although aerobic processes are the most-used for biogas desulfurization, anoxic processes have also been used successfully. These processes use nitrates as electron acceptors according to Equation (8). The most representative species in these processes belong to *Thiobacillus*, *Thialkali*, and *Acidithiobacillus* genera. These bacteria are mesophyllous, can use both molecular oxygen and nitrates as electron acceptors, and can grow in acidic to neutral pH ranges, except for *Thioalkalli vibrio* (Table 9) [3,114]. However, it is often preferable to use alkaline sulfide-oxidizing bacteria capable of growing in a pH range between 10 and 12, since under these conditions, high H_2S loads can be treated, or the size of the desulfurization columns can be minimized in comparison with acid or neutral desulfurization technologies [116].

$$3H_2S + 4NO_3^- \rightarrow 3SO_4^{2-} + 2N_2 + 6H^+ \tag{8}$$

Table 9. Sulfide-oxidizing bacteria in anoxic processes.

Specie	pH	Reference
Thiobacillus denitrificans	6–8	[117,118]
Thiobacillus ferroxidans	2–6	[117,118]
Thioalkali vibrio	7.5–10.5	[119]
Acidothiobacillus ferroxidans	1.6–6	[120]

5.1.3. pH Tolerance

The pH of the culture medium is a crucial parameter for the biogas-upgrading process. CO_2 dissolves in water and can be available mainly as carbonic acid (pH < 6.1), bicarbonate (6.1 < pH < 10.3), or carbonate (10.3 < pH), depending on the pH of the medium. As the pH of the culture medium increases, the solubility of CO_2 is greater, mainly as bicarbonate (or carbonate, depending on the pH)—a chemical species that microalgae efficiently assimilate. Moderately alkalophilic cyanobacteria (pH 8.5–9.4) associated with the genera *Pleurocapsa*, *Synechococcus*, and *Anabaena* have been reported, as well as some highly alkalophilic cyanobacteria (pH > 9.5) associated with the genera *Arthrospira* and *Euhalothece* [121,122], which are promising for biogas-upgrading processes.

5.2. Light Intensity

Microalgae use light as an energy source; therefore, it is a crucial factor that needs to be optimized in microalgae cultivation. Most microalgae use light in the range of 400–700 nm, though the optimal wavelength and intensity will depend on the species. High light intensity inhibits the consumption and assimilation of organic carbon in microalgae with a heterotrophic metabolism.

Chlorophytes are the most-studied microalgae species that simultaneously undergo biogas upgrading and wastewater (or digestate) treatment. In this sense, Zhao et al. [123] reported that red light with an intensity between 1200 and 1600 $\mu mol/m^2/s$ was the most suitable for this purpose, using *Chlorella* sp. However, years later, Ouyang et al. [124] found that moderate light intensities (150–170 $\mu mol/m^2/s^1$) are the most suitable for this purpose in a study that included the strains *S. ubliquus*, *Selenastrum bibraianum*, and *Chlorella* sp. The authors concluded that *S. obliquus* had the best efficiencies. One year later, Yan et al. [125] reported that red light and moderate intensities (400–1000 $\mu mol/m^2/s$) were more suitable for biogas enhancement and the growth of *Chlorella* sp. However, a combination of red and blue light in a 5:5 ratio is preferred for this purpose [62,126,127].

Another critical aspect, in addition to light intensity, is the photoperiod. Yan et al. [126] reported that low intensities (300 $\mu mol/m^2/s$) are more suitable for long photoperiods (16 h light: 8 h dark) for cultures of 0–48 h; moderate intensities (600 $\mu mol/m^2/s$) are more effective in intermediate photoperiods (14 h light: 10 h dark) for 48–96 h cultures; and high intensities (900 $\mu mol/m^2/s^1$) are best for short photoperiods (12 h light; 12 h dark) for 96–144 h cultures.

On the other hand, Wang et al. [128] studied five strains to carry out biogas upgrading, and these were *C. vulgaris*, *S. obliquus*, *Selenastrum capricornutum*, *Nitzschia palea*, and *Anabaena spiroides*. All strains were grown in mono- and co-cultures with activated sludge or fungi. The authors found that co-cultures had better efficiencies in methane upgrading and microalgal biomass production; *S. obliquus* was the microalgae with the best efficiencies.

5.3. Temperature

Temperature is an important factor to consider regarding the photosynthetic activity of algae. Previous studies show that the effect of temperature (between 12 and 35 °C) is negligible in upgrading biogas when a microalgae–bacteria consortium is cultivated in centrate, especially in cultures with high alkalinity (up to 1500 mg/L of inorganic carbon) [84]. On the other hand, Choix et al. [129] and Bose et al. [130] reached the same conclusion, employing temperature ranges of 12–35 °C and 18–37 °C, using the microalgae *Leptolyngbya* sp. CChF1 and *Arthrospira platensis* (Spirulina). However, using a lower temperature for growing microalgae implies less water loss through evaporation and greater CO_2 solubility, especially in cultures with low alkalinity (around 500 mg/L of inorganic carbon) [84].

5.4. Reactor Type

The photosynthetic upgrading of biogas using an external bubble column coupled to an HRAP is the most-used configuration for this purpose, since this is a low-cost technology that is easy to operate and highly effective for large-scale microalgae cultivation [7,55,64,88,91,131].

Co-current feeding for both the biogas and the microalgae culture that enter the bubble column is preferred; it avoids the operational problems of countercurrent feeding, such as obstructions at the top of the column due to sulfur precipitation, pH drops along the bubble column, and the increased removal of dissolved oxygen in the upgraded biogas. Another important factor is the ratio of liquid to gas flows (L/G). However, the results are not conclusive: while some authors suggest that an L/G ratio < 1 allows for obtaining biomethane of the quality required for injection into the natural gas grid [64,131], Rodero et al. [92] reported CO_2 concentrations of up to 12% in upgraded biogas using an L/G ratio of 0.8. However, regardless of the L/G ratio, the removal of CO_2 (and H_2S) from biogas greater than 95% is obtained when using cultures with a pH > 9 [64,88,91].

On the other hand, when the pH of the culture is less than 9, the L/G ratio must increase to guarantee the removal of CO_2. In this sense, Serejo et al. [61] reported that to achieve CO_2 removals greater than 80% using a culture at pH 7.3, it was necessary to use an L/G ratio of 10. Furthermore, although a more-alkaline pH favors the removal of CO_2, it can also increase the extraction of O_2 into the biogas. Likewise, the concentration of microalgae in the absorption column could improve mass transfer in the column, which would translate into better CO_2 removal; however, it was recently reported that increasing the concentration of microalgae in the bubble column did not produce significant differences in CO_2 removal [89]. In addition to this, the photosynthetic activity of microalgae could increase the O_2 content in the improved biogas, compromising its quality.

5.5. Type and Concentration of Nanoparticles

The use of nanomaterials has aroused great interest in recent years since it has been shown that some nanoparticles (NPs) improve the growth (and harvest) of microalgae and/or the accumulation of intracellular compounds, which can be used to obtain biofuels in a later stage [17]. It has been shown that the addition of Fe_2O_3 and SiO_2 NPs (in the range of 100–500 ppm) to the culture medium improves CO_2 fixation by *Chlorella fusca* LEB 111 [13,16,95], as a consequence of an improvement in mass transfer. On the other hand, Ag, Co, and ZnO NPs have been described as having a negative effect when added to microalgae cultures, even at concentrations lower than 1 ppm [132–134]. Furthermore, it has been described that NPs have a hormesis effect in the cultivation of microalgae, so the thresholds of microalgae to NPs are challenging to establish and depend on many factors, such as the species of microalgae, the type and concentration of NPs, the pH of the culture medium, alkalinity, light intensity, etc. [17]. Therefore, it should always be finished experimentally. Recent studies have shown that zero-valent iron NPs coated with carbon improved the productivity of algal biomass and allowed biomethane that could be injected into the natural gas network to be obtained [100,102]. These studies were carried out under controlled lighting conditions—that is, indoors. Therefore, tests abroad must be conducted outdoors to evaluate a more accurate scenario.

6. Perspectives and Challenges

Upgraded biogas is known as biomethane, and there are already established technologies to obtain it; however, operating costs and environmental implications limit its application, so it is necessary to implement more economical and environmentally friendly strategies. One of them is the upgrading of biogas by biological methods, specifically using microalgal cultures, which have already been shown to allow for the upgrading of biogas, achieving biomethane that complies with international regulations.

An option to further improve the efficiency of the biogas-upgrading process is the addition of nanoparticles to the microalgae culture, which also allows for the more significant removal of CO_2 (and H_2S), resulting from an increase in mass transfer, and an improvement in the productivity of algae biomass, which can be used to recover biofuels in a later stage, promoting the circular economy of the process. In this sense, carbohydrates, proteins and lipids are the three main nutritional components of microalgal biomass. Proteins can be used as a nutritional supplement [135]. Lipids are useful for biodiesel production [136], while carbohydrates can be used to obtain alcohols (ethanol and/or butanol) by fermentation [137]. Equally, the entirety of the biomass can be used for biogas production [138]. Although it is true that microalgae can accumulate compounds with very high added value, such as pigments (carotenoids, lutein and others) [139], widely used in cosmetics and pharmacy, more research is needed on the safe application of pigments obtained from microalgae cultivated in wastewater. Therefore, the recovery of energy vectors would be a more attractive option, especially from the point of view of a biorefinery, to make more comprehensive use of microalgal biomass [140], which would also minimize the production of secondary pollutants. However, studies based on lifecycle analysis are needed for these processes, in order to evaluate the environmental impacts associated with obtaining biofuels. In recent years, the use of microalgal biomass as a biofertilizer or biostimulant for plant growth has attracted great interest. Based on a techno-economic and lifecycle analysis, recent studies show that the production of biofertilizers is more feasible than the production of hydrochar [141] or biogas [142] from microalgae, especially when these systems are implemented in regions with warm climates. However, nanoparticles can have an inhibitory effect on the growth of algal biomass, impacting the quality of the biogas. Therefore, it is necessary to experimentally establish, for each microalgae culture, the threshold concentration of the nanoparticle in question they can tolerate.

Figure 3 shows the analysis of co-occurrences based on a bibliometric analysis carried out in VOSviewer 1.6.20 software, from 2000 to date. Seven clusters were identified: cluster 1 (red)—18 items; cluster 2 (green)—13 items; cluster 3 (navy blue)—9 items; cluster 4 (yellow)—8 items; cluster 5 (violet)—7 items; cluster 6 (sky blue)—6 items; and cluster 7 (orange)—2 items. Studies based on "biogas upgrading" are closely related to the topics "microalgae", "biogas", and "anaerobic digestion", since the proximity between the circles, as well as their size, defines the relationship between the keywords. However, the keywords "nanotechnology" and "nanoparticles" show a weaker relationship. To date, few studies have evaluated the use of microalgal–nanoparticle systems for biogas upgrading. In addition, most of the works that use these systems focus on the study of operational parameters that affect the upgrading of biogas, such as pH, alkalinity, L/G ratio, and photoperiod, among others [64,84,88,127,128], and there is little information on the analysis of microbiomes using next-generation high-throughput sequencing technologies, metabolomic analysis, proteomic analysis, and other omics technologies. This would allow us to understand the changes in the microbial community (microalgal and bacterial) and establish the possible interactions between the different species when nanoparticles are added to these systems. Few works exist that study the population dynamics of microalgae present in crops that are used in the biogas-upgrading process. In addition, identification is carried out based on the morphology of the microalgae, which requires highly experienced personnel, since many of the microalgae present polymorphisms. In this sense, molecular techniques represent a more reliable tool for identifying both microalgae and bacteria.

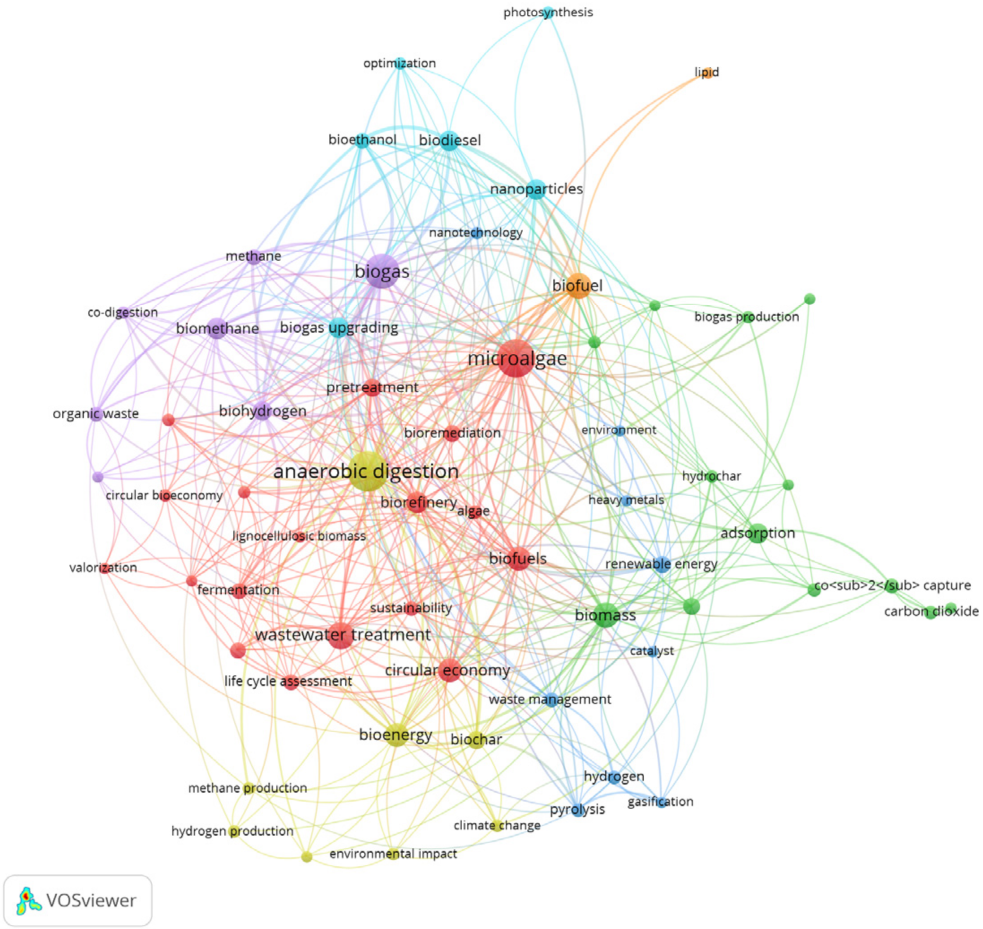

Figure 3. Network visualization of co-occurrence of keywords (https://www.scopus.com; accessed on 17 May 2024).

On the other hand, Figure 4 shows the trend in the study of biogas upgrading based on microalgae–nanoparticle systems. In recent years, there has been a trend in topics related to the "circular bioeconomy" or "environmental impacts", which means that the need arises to carry out the lifecycle analysis of these systems in order to evaluate these processes more comprehensively, to study the economic, environmental and social impacts. To date, several studies have demonstrated the impact of NPs in improving microalgae growth, as well as in their harvest [143]. However, a techno-economic and environ-mental impact analysis of these systems is still lacking, since the repercussions that the accumulation of NPs may have on the environment are unknown. Another option would be to implement a strategy to recover and reuse them in order to minimize their incorporation into the environment. Recent studies have experimentally demonstrated that, at low concentrations, nanoparticles are capable of improving the physiological processes of plants [144,145]. However, the physicochemical properties (metal used, shape, size and surface chemistry) of NPs will be decisive for their safe use as fertilizers. Previous studies have reported that the addition of ZnO NPs (1000 mg/kg) improves corn growth. It has been reported that TiO2 NPs in the range 1–100 mg/kg do not inhibit the growth of the soil bacterial community, while Ag and CuO NPs are toxic to the soil bacterial community in comparable concentrations [146], compromising plant growth. However, the doses used vary greatly depending on the type of NP, the type of plant, the application mode and environmental conditions.

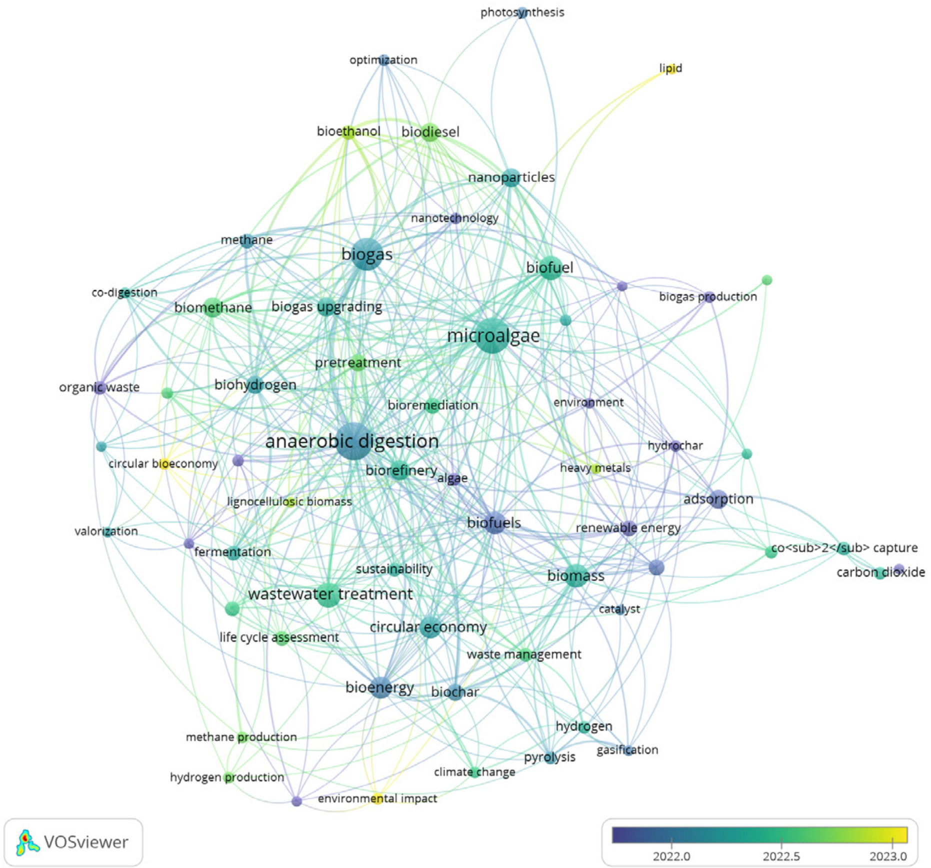

Figure 4. Overlay visualization of co-occurrence of keywords plus (https://www.scopus.com; accessed on 17 May 2024).

The magnetic flocculation of microalgae using magnetic NPs (magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3)) has been reported as a fast, simple and potentially sustainable harvesting method [147]. However, NP production and functionalization account for the majority of material costs, i.e., bare iron oxides cost approximately USD 50–200/g. However, large-scale in-house synthesis can dramatically reduce this price to USD 0-1-0.30/g [143,148], which would be even more attractive if NP synthesis was performed using green chemistry. This involves using aqueous extracts based on plants, algae or microorganisms for the reduction and/or stabilization of nanoparticles from a precursor. This prevents the use of toxic reagents used in the chemical synthesis of nanoparticles, allowing the revaluation of waste and improving the economy of the process. Considering the costs of the microalgae harvesting stage, it is estimated that magnetic separation would cost 0.07–0.16 USD/kg of algae, which is competitive with other harvesting methods such as centrifugation, filtration and flocculation [148]. In addition to this, the magnetic characteristics of some NPs facilitate their recovery and reuse, further reducing costs and promoting a more economical and friendly process. However, since these systems (of microalgae and nanoparticles) are emerging technologies for biogas upgrading, to date, there are no techno-economic and lifecycle studies that support the feasibility of these systems, which represents an area of opportunity.

7. Conclusions

Biogas upgrading using a microalgae–nanoparticle system is a more sustainable process than conventional technologies since it simultaneously allows for biogas upgrading and the production of biomass, which can be used to obtain biofuels, improving the economy of the process. However, it is necessary to implement molecular techniques, such as next-generation sequencing, to study the microbiome of these systems further. In addition, incorporating other study tools, such as lifecycle analysis, is essential to evaluate these upgrading processes from a more comprehensive point of view.

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Data Availability Statement: Figure 1: data were obtained from the period between 1999 and 2024 (https://www.sciencedirect.com; accessed on 10 May 2024). Figures 3 and 4: data were obtained from https://www.scopus.com; accessed on 17 May 2024.

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