Chemosphere 321 (2023) 138084

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Recent advances in biological technologies for anoxic biogas desulfurization

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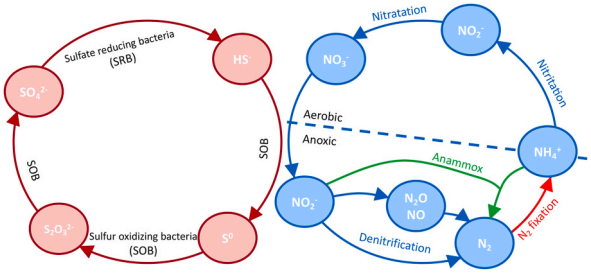
HIGHLIGHTS

- Anoxic biodesulfurization is a rising process given its high elimination capacities.
- Simultaneous removal of H_2S from biogas and NH_4^+ from other effluents is enabled.
- The use of suspended growth and fixed biomass bioreactors is possible.
- The oxidation product (S^0/SO_4^{2-}) is mainly determined by the nitrogen-sulfur ratio.
- The technology was recently validated at TRL 7 but more studies are needed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Handling Editor: Dr A ADALBERTO NOYOLA

Keywords:
Biodesulfurization
Sulfide
Nitrification
Bioreactor
Microbial
Biotrickling filter

ABSTRACT

Recovery of the energy contained in biogas will be essential in coming years to reduce greenhouse gas emissions and our current dependence on fossil fuels. The elimination of H_2S is a priority to avoid equipment corrosion, poisoning of catalytic systems and SO_2 emissions in combustion engines. This review describes the advances made in this technology using fixed biomass bioreactors (FBB) and suspended growth bioreactors (SGB) since the first studies in this field in 2008. Anoxic desulfurization has been studied mainly in biotrickling filters (BTF). Elimination capacities (EC) up to 287 gS m^{-3} h^{-1} have been achieved, with a removal efficiency (RE) of 99%. Both nitrate and nitrite have been successfully used as electron acceptor. SGBs can solve some operational problems present in FBBs, such as clogging or nutrient distribution issues. However, they present greater difficulties in gas-liquid mass transfer, although ECs of up to 194 gS m^{-3} h^{-1} have been reported in both gas-lift and stirred tank reactors. One of the major disadvantages of using anoxic biodesulfurization compared to aerobic biodesulfurization is the need to provide reagents (nitrates and/or nitrites), with the consequent increase in operating costs. A solution proposed in this respect is the use of nitrified effluents, some ammonium-rich effluents nitrified include landfill leachate and digested effluent from the anaerobic digester have been tested successfully. Among the microbial diversity found in the bioreactors, the genera *Thiobacillus*, *Sulfurimonas* and *Sedimenticola* play a key role in anoxic removal of H_2S. Finally, a summary of future trends in technology is provided.

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https://doi.org/10.1016/j.chemosphere.2023.138084
Received 13 October 2022; Received in revised form 11 January 2023; Accepted 5 February 2023
Available online 10 February 2023
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CRediT author statement

Joaquín González-Cortés: Conceptualization, Writing - original draft, Writing- Reviewing and Editing. **Fernando Almenglo**: Conceptualization, Writing - original draft, Writing- Reviewing and Editing. **Martín Ramírez**: Conceptualization, Funding acquisition, Project administration, Writing - original draft, Writing- Reviewing and Editing. **Domingo Cantero**: Writing- Reviewing and Editing.

1. Introduction

Biogas is a renewable energy source produced by the biodegradation of organic matter under anaerobic conditions that essentially comprises CH_4 (45–75%) and CO_2 (20–50%) (Ramírez et al., 2015). However, its composition is highly variable given the wide variability of organic substrates, such as food waste, microalgae, sewage sludge, agricultural waste, livestock manure, industrial waste, organic fraction of municipal solid wastes, etc., that can be used for its production (Chong et al., 2021; Di Capua et al., 2020; Huynh Nhut et al., 2020; Khanongnuch et al., 2019a). Moreover, several minor compounds, such as H_2, O_2, N_2, NH_3, H_2S, volatile organic compounds (VOCs) and siloxanes, among others, may also be present. The presence of these minor compounds is not always detrimental since it will depend on the final use of biogas, but in most cases, it is essential to eliminate or reduce the concentration of H_2S due to it is considered the most toxic and corrosive compound and its presence can hinder the biogas usage (Habeeb et al., 2018). H_2S concentrations vary, with a typical range of 0.1–1% (Ramírez et al., 2015), although much higher concentrations are possible. For example, the treatment of sulfate-laden wastewater, such as vinasse from the sugarcane industry, can generate biogas with an H_2S concentration of up to 3% (Colturato et al., 2016). One of the main uses of biogas is combustion in cogeneration engines, where the H_2S concentration needs to be reduced below 0.013% (Deublein and Steinhauser, 2008). Nevertheless, other uses are also possible, such as injection into the natural gas grid, vehicle fuel production, fuel source for solid-oxide fuel cells, production of H_2 by biogas reforming, among others. (Chouhan et al., 2021; Katariya and Patolia, 2021). In these cases, higher purification requirements or even CO_2 removal (biogas upgrading) are essential.

There is worldwide concern for the use of renewable energy sources in order to reduce greenhouse gas (GHG) emission and our dependence on fossil fuels. The Paris Agreement sets out a global framework to reduce global warming (UNFCCC, 2015) in which the signatories are committed to reducing GHG emissions by at least 40% by 2030 compared to 1990. In the EU, the 2030 climate and energy framework targets at least 55% of net GHG emission by 2030: 40% cuts in GHGs, 32% share for renewable energy and 32.5% improvement in energy efficiency. In addition, the EU aims to be climate-neutral by 2050 (European Union, 2020). In the recent Glasgow Climate Pact, adopted at the COP26 UN climate conference (November 2021), it was recognized that limiting the rise in global warming to 1.5 °C requires a rapid, deep and sustained reduction in GHG emissions, with a 45% net reduction by 2030 relative to the 2010 level and net zero by 2050, as well as significant reductions in other GHGs, such as methane (UNFCCC, 2021). The Global Methane Pledge aims to reduce international methane emissions (Climate and clean air coalition, 2021) to avoid eight gigatons of CO_2 equivalent emission by 2030. As such, energy recovery from biogas is essential for reducing GHG emissions and our dependence on fossil fuels. According to data published by EurObserv'ER (2020), biogas production in the EU28 was 16.6 Mtoe (Million tonnes of oil equivalent), the number of biomethane plants in 2019 was 729, and there were a total of 18,202 biogas-producing plants in 2018. The main issues related to the presence of H_2S in biogas are equipment corrosion, poisoning of catalytic systems and SO_2 emissions in combustion systems. Thus, a large number of biogas desulfurization technologies have been developed, with the most widespread being physicochemical (alkanolamine scrubber, impregnated activated carbon, iron chloride dosage, etc.) (Awe et al., 2017; Okoro and Sun, 2019; Ramírez et al., 2015). Biological technologies, which have traditionally been aerobic, are an alternative to physicochemical ones. There are many configurations based on aerobic biological processes, which include biotrickling filters (BTFs) (Juntranapaporn et al., 2019; López et al., 2016), the Thiopaq® process (Janssen et al., 2009), and the Bio-SR process (Lin et al., 2013; Mesa et al., 2004; Satoh et al., 1988), etc.

Anoxic processes have attracted the attention of researchers recently as they have the advantage of avoiding biogas dilution and explosion risks. Anoxic desulfurization comprises a series of physical (advection, absorption, diffusion) and biological (biodegradation) mechanisms, in which H_2S is transferred from the biogas to the microorganism where it is used as an electron donor by chemoautotrophs and biotransformed to SO_4^{2-} and/or S^0 (Almenglo et al., 2016c). As an electron acceptor, the use of both nitrate and nitrite has been described instead of O_2, used in aerobic biodesulfurization. Moreover, the use of a nitrified effluent as the nitrate or nitrite source reduces operating costs (Cano et al., 2018) and allows two streams to be treated simultaneously: sour biogas (in an anoxic bioreactor) and ammonium-rich wastewater (in a nitrification bioreactor) (González-Cortés et al., 2021a).

Biological technologies (both aerobic and anoxic) present a much lower environmental impact than physico-chemical technologies. Despite aerobic biodesulfurization being the most favorable technology to desulfurize biogas from an environmental perspective, if we consider that a nitrification bioreactor is already built the anoxic biofiltration is more favorable in many environmental impacts categories such as human toxicity, terrestrial acidification, water depletion or climate change (Cano et al., 2018). From an economical point of view, the presence of a previous nitrification bioreactor is a key factor to choose between aerobic or anoxic biogas biodesulfurization (Cano et al., 2018). Biogas dilution is the main drawback of the aerobic process especially if the desulfurized biogas is intended to be upgraded to biomethane due to the increasing downstream efforts to remove N_2 and O_2. In that scenario, the anoxic process emerges as the main biological alternative to physical-chemical to perform the desulfurization of biogas.

The first studies regarding anoxic desulfurization were published in 2008 (Soreanu et al., 2008a, 2008b, 2008c), and since then they have increased in number to a total of around 100 (Fig. 1a). From 2010 to the time of this article, and based on the search criteria used (Fig. 1a), anoxic desulfurization studies represent an average of 33 ± 2% of all studies compared with aerobic ones. The number of publications per year since 2010 has remained approximately constant, with an average of 8 ± 2 and a maximum of 12 in 2014. Most of them have been carried out by Spanish universities (43), followed by institutions from China (15), Brazil (9), Canada (8), and Mexico (8), etc. (Fig. 1b). Most of these studies were conducted on a laboratory scale (Brito et al., 2018; Cano et al., 2019; Fernández et al., 2013; Khanongnuch et al., 2019a; Xu et al., 2020), although some pilot-scale studies have also been carried out (Almenglo et al., 2016a, 2016b; 2016c; Gamisans et al., 2021; Zeng et al., 2019). There are a large number of studies using biotrickling filters under anoxic conditions, but it is also possible to find other configurations, such as stirred tank bioreactors (González-Cortés et al., 2021b), gas-lift (González-Cortés et al., 2021a), bubble columns (Deng et al., 2009), horizontal-flow packed bed (de Bello Solcia Guerrero et al., 2020), etc.

This review aims to summarize and analyze all the advances achieved from 2008 until the present in anoxic biogas desulfurization. Although there are many types of bioreactors, they have been classified into two groups: suspended growth bioreactors (SGB) and fixed-biomass bioreactors (FBB). Moreover, a section has been dedicated to a discussion of experimental configurations that combine anoxic desulfurization with the nitrification of ammonium-rich effluents. After reviewing the different types of bioreactors, all studies characterizing the microbial consortia present in these bioreactors are discussed. Finally, a brief analysis of future trends in this field is provided. We hope that this review will be useful to all researchers currently working in the field to

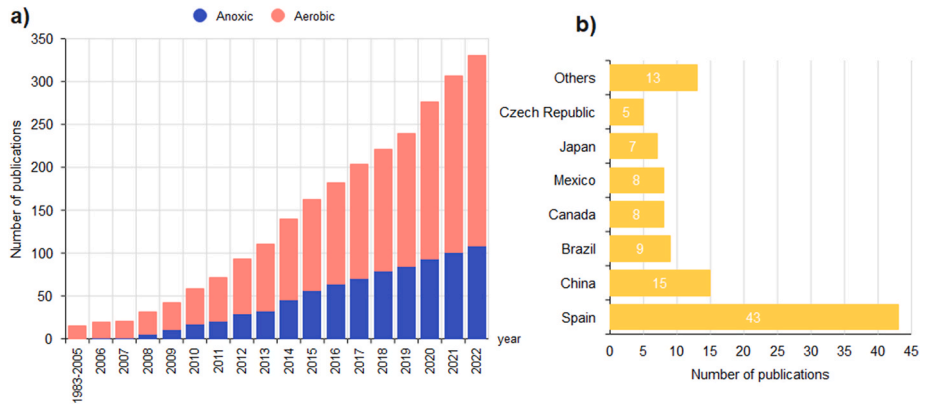

Fig. 1. a). The cumulative number of publications containing either the concept: Anoxic (blue) – "anoxic biogas hydrogen sulfide removal" or "anoxic biogas desulfurization"; aerobic (orange) – "oxygen biogas hydrogen sulfide removal" or "oxygen biogas desulfurization". b). The total number of publications per country for the previous anoxic search [Scopus, accessed 10.11.22].

help identify technology gaps. It may also be of great interest to all stakeholders involved in biogas use, as it will allow them to analyze the state of the art of anoxic desulfurization technologies.

2. Fixed-biomass bioreactors

Anoxic biodesulfurization has traditionally been performed in BTFs in which biomass is immobilized on an inert solid carrier. Indeed, numerous studies have demonstrated the robustness, high elimination capacities (ECs), and cost-effectiveness of BTFs (Cano et al., 2019; Khanongnuch et al., 2019b; Zeng et al., 2018). Despite all the advantages stated above, a common shortcoming of their use is the accumulation of biomass and/or elemental sulfur on the packing material, which can result in clogging. This aggregation causes high pressure drops and system flooding, which results in the need for frequent operational shut-downs and high maintenance costs (Almenglo et al., 2016b; Qiu and Deshusses, 2017).

2.1. Biotrickling filters

A BTF is a type of biofilter in which an aqueous solution containing nutrients percolates continuously through the packing bed (Fig. 2). A brief summary of the main operational parameters and performance of the bioreactors used to perform anoxic desulfurization is provided in Table 1. The efficiency and performance of the BTF will depend on several factors, which may be physical, such as trickling liquid velocity (TLV), packed bed height-diameter ratio, etc., or related to the biological degradation rate, such as HS^-, NO_3^- and NO_2^- concentration, biomass distribution along the bed, community composition, etc.

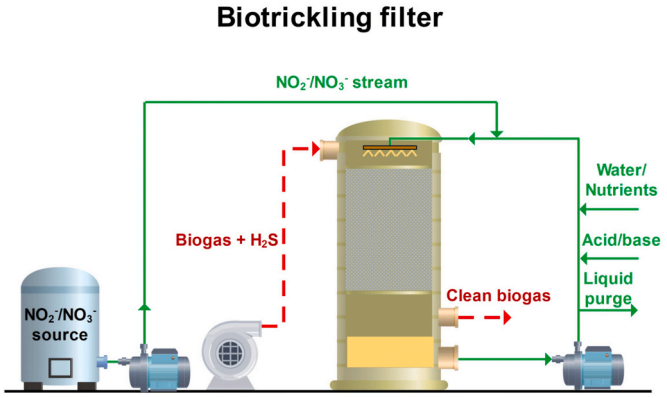

Fig. 2. Anoxic biotrickling filter configuration under co-current flow mode.

Nitrate or nitrite can be used as the final electron acceptor instead of oxygen. This nitrate or nitrite can be obtained from a commercial supplier (chemical source) or be produced in a nitrification bioreactor by the biological oxidation of ammonium-rich effluent (biogenic source) (González-Cortés et al., 2021a). However, it is important to note that when O_2 is present in biogas, the addition of nitrate or nitrite as an electron acceptor is not necessary if the H_2S concentration present in biogas is low. In these conditions, aerobic biodesulfurization takes place (Poser et al., 2022).

Anoxic desulfurization has been mostly studied in BTFs. This configuration has certain advantages such as the ease of converting chemical scrubbers into BTFs, good retention of slow growing microorganism, single reactor configuration and good control of pH (Almenglo et al., 2016c; Fernández et al., 2013; Gabriel and Deshusses, 2003; González-Cortés et al., 2021b; Rodriguez et al., 2014; Santos et al., 2015). Furthermore, the continuous trickling in BTFs performing the anoxic desulfurization favors nitrate and/or nitrite distribution due to the presence of the electron acceptor dissolved in water (Almenglo et al., 2016c).

2.2. Operational considerations

It is common to characterize the behavior of the BTF in terms of the critical elimination capacity (EC_{CRIT}). This term represents the EC when the removal efficiency (RE) is close to 100% and, depending on the study, this value is typically between 95% and 99%. As shown in Table 1, it is common to find authors reporting an EC_{CRIT} above 100 gS-H_2S m^{-3} h^{-1} on both a laboratory (Brito et al., 2019, 2018, 2017; Cano et al., 2021, 2019; Fernández et al., 2014, 2013) and a pilot scale (Almenglo et al., 2019; Turker et al., 2012).

Fig. 3 represents the IL and H_2S inlet concentration values reported in literature with a RE>95% as a function of EBRT. It allows discerning the area of application of desulfurization by anoxic BTF and a quick estimation of the reactor size. Above an IL of 294.6 gS m^{-3} h^{-1} and an inlet concentration of 10,000 ppm_V no experimental data have been reported so these values were considered as the upper limit.

2.2.1. Nitrogen oxidation state and product selectivity

Anoxic desulfurization occurs simultaneously with a denitrification process (eq. (1)). Anoxic desulfurization is a two-step process in which H_2S is firstly oxidized to elemental sulfur, which can then be further oxidized to sulfate (Mora et al., 2015). From an operational point of view, partial desulfurization (eqs. (2)–(4)) or total desulfurization (eqs. (5)–(7)) is usually considered (Qaisar Mahmood et al., 2007; Soreanu et al., 2008b). As such, it is possible to relate how the ratio of nitrate or nitrite to H_2S influences the product of the desulfurization reaction

Table 1
Main operational parameters and performance in studies for anoxic desulfurization of biogas.

Type	Scale [Volume]	$[H_2S]_{IN}$ [ppm_V]	EC_{CRIT} [gS m^{-3} h^{-1}] (RE %)	EC_{MAX} [gS m^{-3} h^{-1}] (RE %)	EBRT/GRT [min]	pH	N_{source}	N feeding	REF
BTF	Laboratory [12 L]	1100 ± 300	9.3 (100%)	16.5 (66%)	10.2–72	6–7	Biogenic + chemical NO_3^-	Continuous	Soreanu et al. (2008a)
BTF	Laboratory [12 L]	1100 ± 300	4.9 (100%)	4.9 (100%)	18	6.5	Biogenic + chemical NO_3^-	Batch	Soreanu et al. (2008b)
BTF	Laboratory [14 L]	–	12.5 (95%)	12.5 (95%)	12–85	5.8–6.3	Biogenic + chemical NO_3^-	Continuous	Soreanu et al. (2008c)
BBC	Laboratory [3.9 L]	1000–1500	4.3 (95%)	16.2 (90%)	1.1–15.7	8.1–8.4	Biogenic NO_3^- + NO_2^-	Continuous	Deng et al. (2009)
BTF	Laboratory [12 L]	2000–4000	–	–	9–62	6.5	Biogenic + chemical NO_3^-	Continuous	Soreanu et al. (2010)
Other[a]	Pilot [2.4 m^3]	30000–35000	166 (>95%)	570 (87%)	2.8–14.4	6.5–8	Biogenic NO_3^- + NO_2^-	Continuous	Baspinar et al. (2011)
HFBR	Pilot [26.5 L]	20000	31.25 (>99%)	31.25 (>99%)	21.2	7	Biogenic NO_3^- + NO_2^-	Continuous	Chinalia et al. (2012)
BTF	Laboratory [2.3 L]	426–2594	84.7 (98%)	142.0 (47%)	0.5–3	7.4–7.5	Chemical NO_3^-	Continuous	Montebello et al. (2012)
Other[a]	Pilot [2.4 m^3]	30000–35000	–	204 (94%)	15	7.3–8	Biogenic NO_3^- + NO_2^-	Continuous	Turker et al. (2012)
BTF	Laboratory [2.4 L]	1400–14600	120 (99%)	170 (84%)	2.4–15	7.4–7.5	Chemical NO_3^-	Batch	Fernández et al. (2013)
BTF	Laboratory [2.4 L]	850–8500	130 (99%)	171 (84%)	2.4–4.3	6.8–7.5	Chemical NO_3^-	Batch and continuous	Fernández et al. (2014)
FBS	Laboratory [20 L]	2300–9400	6.03 (99%)	7.05 (45%)	0.5	–	Chemical NO_3^-	Continuous	Pokorna et al. (2015)
BBC	Laboratory [3.35 L]	1400–1900	–	–	–	–	Biogenic NO_3^-	Batch	Wang et al. (2015)
BTF	Pilot [166 L]	4000–4500	56 gS- (98%)	56 (98%)	1.9–10	7.4	Chemical NO_3^-	Batch	Almenglo et al. (2016a)
BTF	Pilot [166 L]	4000–4500	37.9 (99%)	37.9 (99%)	–	7.4	Chemical NO_3^-	Continuous	Almenglo et al. (2016a)
BTF	Pilot [166 L]	4100–7900	94.7 (>99%)	127.3 (92.6%)	2.9–10	7.4	Chemical NO_3^-	Batch and continuous	Almenglo et al. (2016b)
FBS	Laboratory [250 mL]	7000	22 (98%)	22 (98%)	*HRT: 4 h*	8–9	Chemical NO_3^-	Continuous	Bayrakdar et al. (2016)
BTF	Laboratory [2.5 L]	5000–12000	26.0 (98.4%)	26.0 (98.4%)	30–79	7	Chemical NO_3^-	Batch	Lebrero et al. (2016)
BTF	Pilot [43 L]	100–1600	1.79 (99.3%)	8.15 (96.4%)	4.1–20.5	6.2–6.8	Chemical NO_3^-	Batch	Ziemiński and Kopycki (2016)
BTF	Laboratory [0.25 L]	1600	24.9 (99.6%)	51.29 (100%)	5	7.5–8	Chemical NO_3^-	Continuous	Li et al. (2016)
BBC	Laboratory [0.25 L]	1600	24.85 (99.4%)	24.85 (99.4%)	6	7.5–9	Chemical NO_3^-	Continuous	Li et al. (2016)
BTF	Laboratory [2.8 L]	710–3564	137 (97%)	137 (97%)	1.9	7.4	Chemical NO_3^-	Continuous	Brito et al. (2017)
BF	Laboratory [7.85 L]	25–1100	25.2 (100%)	30.3 (80%)	1–5	7–9	Chemical NO_3^-	Batch	Jaber et al. (2017)
BTF	Laboratory [1 L]	5000	8 (100%)	8 (100%)	60	6.9	Chemical NO_3^-	Continuous	López et al. (2017)
BTF	Laboratory [2.8 L]	710–3564	137 (97%)	137 (97%)	1.9	7.4	Chemical NO_3^- and NO_2^-	Batch and continuous	Brito et al. (2018)
BTF	Laboratory [2.8 L]	710–3564	135.8 (96%)	135.8 (96%)	1.9	7.4–7.5	Chemical NO_3^-	Continuous	López et al. (2018)
BTF	Laboratory [0.6 L]	80–2300	5.24 (99%)	5.24 (99%)	–	6.6–8.1	Biogenic NO_3^-	Continuous	Tanikawa et al. (2018)
BTF[b]	Laboratory [5 L]	2000	17.5 (96%)	30.67 (84.7%)	7	7	Chemical NO_3^- and Biogenic NO_3^- + NO_2^-	Continuous	Zeng et al. (2018)
BTF	Pilot [166 L]	4100–5100	106 (97.6%)	158 (92.1%)	2–10	7.4	Chemical NO_3^-	Batch	Almenglo et al. (2019)
BTF	Laboratory [2.8 L]	710–3564	137 (97%)	137 (97%)	1.1–1.9	7.4	Chemical NO_2^-	Continuous	Brito et al. (2019)
BTF	Laboratory [2.8 L]	2000–10000	287.5 (99%)	287.5 (99%)	0.5–2.7	7.3–7.5	Chemical NO_3^-	Continuous	Cano et al. (2019)
BTF	Laboratory [2.1 L]	100–500	19.2 (96%)	19.2 (96%)	3.5	7 +-2	Chemical NO_3^-	Continuous	Khanongnuch et al. (2019c)
BTF	Laboratory [2.1 L]	98–116	16 (100%)	37.8 (93.9%)	0.9–3	7.7–8.3	Chemical NO_3^-	Continuous	Khanongnuch et al. (2019b)
BTF[b]	Laboratory [11.4 L]	5000	–	81.2 (94.5%)	5.7–28.5	6–8	Biogenic NO_3^- + NO_2^-	Continuous	Zeng et al. (2019)
BTF	Laboratory [2.8 L]	1900	–	94.73 (94%)	1.9	7.4	Chemical NO_3^- and NO_2^-	Continuous	Brito et al. (2020)
HFBR	Laboratory [1.2 L]	100–1600	–	18.7 (64.2%)	1.2–3	7.4–8.2	Biogenic NO_3^- + NO_2^-	Continuous	(de Bello Solcia Guerrero et al., 2020)
Other[c]	Laboratory [0.4 L]	450–1100	–	10.2	0.5	5.7–8.8	Biogenic NO_3^- + NO_2^-	Continuous	(de Bello Solcia Guerrero et al., 2020)

(*continued on next page*)

Table 1 (*continued*)

Type	Scale [Volume]	$[H_2S]_{IN}$ [ppm_V]	EC_{CRIT} [gS m^{-3} h^{-1}] (RE %)	EC_{MAX} [gS m^{-3} h^{-1}] (RE %)	EBRT/GRT [min]	pH	N_{source}	N feeding	REF
BTF	Laboratory [0.81 L]	210–2550	1.3 (100%)	10.6 (80%)	23	7.8	Chemical NO_3^-	Batch and continuous	Dupnock and Deshusses (2020)
Gas-lift	Laboratory [3 L]	853–3500	177 (99%)	194 (84%)	2–0.68	7.4–7.8	Chemical NO_2^-	Batch and continuous	González-Cortés et al. (2020)
BTF	Laboratory [3 L]	100–4000	113.5 (97%)	113.5 (97%)	3	7–8	Chemical NO_3^-	Fed-batch and continuous	Watsuntorn et al. (2020)
BTF	Laboratory [2.8 L]	0–5210	119.5 (99.1%)	151.9 (97.3%)	2.6	7.3–7.5	Biogenic NO_3^- + NO_2^-	Continuous	Cano et al. (2021)
CSTBR	Laboratory [5.5 L]	900–4500	99 (99%)	194 (72%)	2.32–0.68	7.8	Chemical NO_2^-	Batch and continuous	González-Cortés et al. (2021b)
Gas-lift	Laboratory [3 L]	860–1300	134 (95%)	134 (95%)	1.73–0.68	7.8	Biogenic NO_3^- + NO_2^-	Continuous	González-Cortés et al. (2021a)
BS	Laboratory [1.3 L]	2500–10000	31.9 (97.5%)	50.73 (95.6%)	13–16	7	Chemical NO_3^-	Continuous	Flores-Cortés et al. (2021)
BBC	Pilot [50 L]	335–562	–	13.37 (90.7%)	2.8–14.4	5–7.3	Biogenic NO_3^- + NO_2	Continuous	Sempere et al. (2022)
HFMB	Laboratory [–]	63–1854	152.1 (97%)	162 (87%)	0.7–.3.1	3.5–7	Biogenic NO_3^- + NO_2	–	Das et al. (2022)

[a] Hybrid biological bubble column and scrubber tower.
[b] Biotricking filter with a flooded part.
[c] Anoxic vertical fixed-bed reactor.

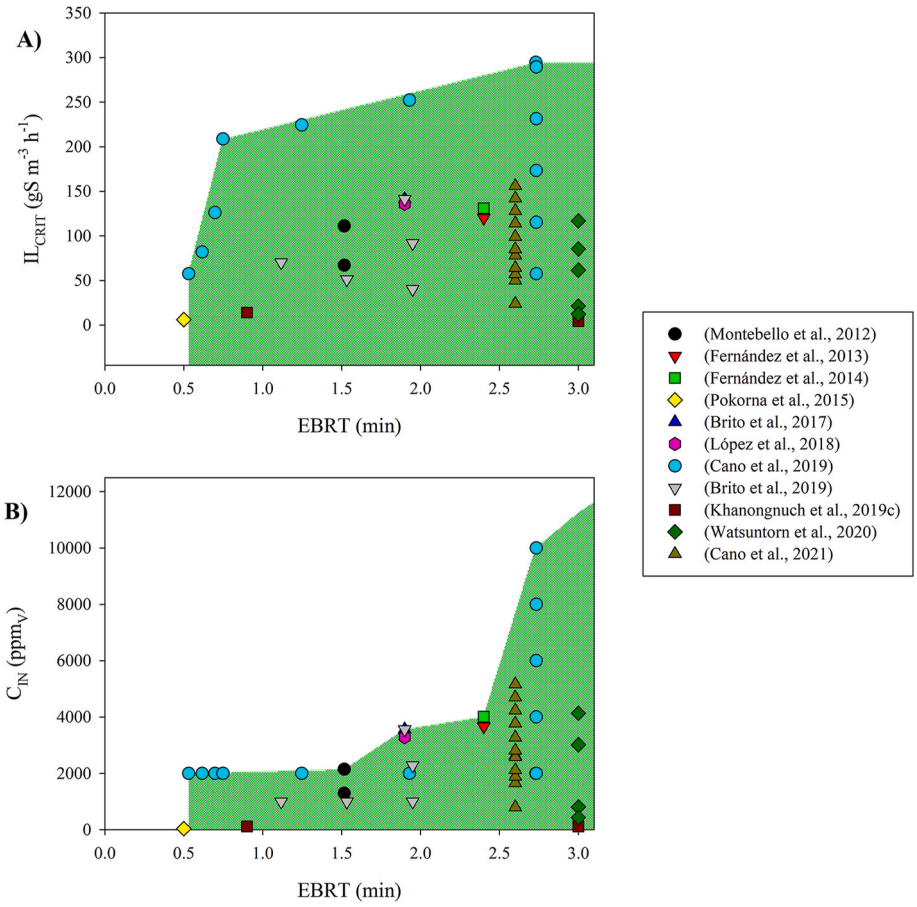

Fig. 3. Critic inlet load (A) and H_2S concentration (B) as a function of the empty bed residence time. All the represented values were obtained using biotrickling filters obtaining a removal efficiency over 95%. The area represents the scenarios in which the anoxic desulfurization can be applied.

(sulfate and/or elemental sulfur). This ratio is usually expressed as the N/S molar ratio between nitrate and/or nitrite (expressed as nitrogen) and H_2S (expressed as elemental sulfur).

When feeding a mixture of nitrite and nitrate, it is possible to express the concentration of the mixture as nitrate equivalents (González-Cortés et al., 2021a), as shown in equation (8). This equation takes into account the lower oxidizing capacity of nitrite by weighting its concentration using the adjustment factor "a", and can be calculated from linear regression between nitrate and nitrite concentration using kinetic equations or by minimizing the error between experimental and

estimated sulfate (Cano et al., 2021). The kinetics described in equations (2), (4), (5) and (7) give an "a" value of 1.66, whereas the kinetics described by Mora et al. (2015) gives a value of 1.91 and Cano et al. (2021) found an experimental value of 1.6. This simplification has been useful to predict product selectivity. Certain key operational aspects such as reagent consumption, pH control, inhibition by products or the maintenance of the fixed beds are intimately linked to the biological reaction products (Almenglo et al., 2016a; Bayrakdar et al., 2016; Cano et al., 2018, 2019; Feng et al., 2021; González-Cortés et al., 2020; Jaber et al., 2017; Lebrero et al., 2016; López et al., 2018). However, more studies are needed addressing its feasibility from an economic and operational point of view. The influence of the N/S molar ratio on the reaction product has been investigated by several authors (Almenglo et al., 2016a, 2016b; Brito et al., 2020, 2018, 2017; Cano et al., 2019; Fernández et al., 2014, 2013; López et al., 2018; Soreanu et al., 2008a, 2008b), who have found some deviations from the theoretical equations. When total denitrification does not occur, the product selectivity is more complex to estimate as all stoichiometric equations (2)–(7) have to be considered.

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2 \quad (1)$$

$$5H_2S + 2NO_3^- \rightarrow 5S^0 + N_2 + 4H_2O + 2OH^- \quad (2)$$

$$H_2S + NO_3^- \rightarrow S^0 + NO_2^- + H_2O \quad (3)$$

$$3H_2S + 2NO_2^- + 2H^+ \rightarrow 3S^0 + N_2 + 4H_2O \quad (4)$$

$$5H_2S + 8NO_3^- \rightarrow 5SO_4^{2-} + 4N_2 + 4H_2O + 2H^+ \quad (5)$$

$$H_2S + 4NO_3^- \rightarrow SO_4^{2-} + 4NO_2^- + 2H^+ \quad (6)$$

$$3H_2S + 8NO_2^- + 2H^+ \rightarrow 3SO_4^{2-} + 4N_2 + 4H_2O \quad (7)$$

$$[NO_3^-]_{eq} = [NO_3^-] + \frac{[NO_2^-]}{a} \quad (8)$$

When complete denitrification (i.e. when N_2 is the final product) occurs, the complexity decreases and simple expressions can be proposed to estimate the product selectivity. Some experimental fittings (Almenglo et al., 2016a; Brito et al., 2018; Fernández et al., 2013; López et al., 2018) using nitrate and nitrite are given in equations (9)–(12), respectively.

$$\frac{g\ S - SO_4^{2-}}{g\ S - H_2S_{removed}} = -0.1041 + 0.5328 \bullet N/S_{removed} \quad (9)$$

$$\frac{g\ S - SO_4^{2-}}{g\ S - H_2S_{removed}} = +0.0212 + 0.5328 \bullet N/S_{removed} \quad (10)$$

$$\frac{g\ S - SO_4^{2-}}{g\ S - H_2S_{removed}} = -0.0441 + 0.5328 \bullet N/S_{removed} \quad (11)$$

$$\frac{g\ S - SO_4^{2-}}{g\ S - H_2S_{removed}} = +0.0193 + 0.3717 \bullet N/S_{removed} \quad (12)$$

A low N/S molar ratio has little effect on the RE when using BTFs (Cano et al., 2019). Thus, Cano et al. (2019) fed very low N/S molar ratios ranging between 0.343 and 0.409 mol mol^{-1} at inlet load (IL) of between 115.2 and 289.3 gS-H_2S m^{-3} h^{-1}, and obtained REs of 93–97% under counter-current and 90–96% when working in co-current mode. Sulfate selectivity was higher in co-current (12.4%) than in counter-current mode (2.4%). Co-current flow can allow a better depletion of nitrate and lower elemental sulfur production (Cano et al., 2019) due to contact between the highest H_2S concentration and nitrate or nitrite concentrations at the top of the column. Moreover, alternative operation switching between both mode flows can enhance the packing material (open polyurethane foam (OPUF)) lifetime due to a better distribution of biomass and elemental sulfur (Almenglo et al., 2016a).

The effect of switching between both electron acceptors (nitrate to nitrite and vice versa) on BTF performance has also been studied (Brito et al., 2018, 2020). The switch in electron acceptor was performed in a BTF at a constant IL of 78.8 gS-H_2S m^{-3} h^{-1} and a feedback control that kept the outlet H_2S concentration constant at 100 ppm_v. While the change from nitrate to nitrite did not affect the RE, the consumed N/S molar ratio increased from 1 to 1.3 mol mol^{-1} and sulfate production increased from 25% to 46%. After 68 days of feeding nitrite, the BTF became adapted to the new electron acceptor, with the consumed N/S molar ratio decreasing from 1.3 to 0.69, which caused a decrease in sulfate selectivity to 20%. Furthermore, Brito et al. (2020) did not observe a reduction in the RE when changing the electron acceptor from nitrite to nitrate and vice versa.

Sulfide concentration is a factor that can affect the selectivity of the reaction product in the anoxic BTF. It should be noted that the oxidation kinetics of elemental sulfur to sulfate is inhibited by high sulfide concentration in the liquid. Mora et al. (2015) described it using a noncompetitive inhibition term. Thus, Almenglo et al. (2016b) found how an increase in the IL (from 45 to 110 gS-H_2S m^{-3} h^{-1}) resulted in decrease in sulfate production (from 17% to 8%) or how an increase in pH (from 6.8 to 7.4), and a subsequent increase in H_2S solubility, reduced sulfate production from 69% to 40%. Jaber et al. (2017) increased the inlet H_2S concentration from 150 to 600 ppm_v at a constant fed N/S molar ratio of 0.89 mol mol^{-1}. The increase in IL at the same N/S molar ratio led to a reduction in sulfate production from 90% to 59% using a BTF packed with expanded schist.

2.2.2. Physicochemical considerations

pH has an effect on both microbial activity and the mass transfer rate of H_2S from the gas phase to the liquid medium. H_2S is a polyprotic acid the dissolution of which in water leads to dissociation into bisulfide ion (HS^-) and sulfide ion (S^{2-}) (eq. (13)). The equilibrium between gaseous H_2S concentration and liquid sulfide, considering both undissociated and dissociated species, can be expressed using a dimensionless gas-liquid equilibrium constant (eq. (14)) (Almenglo et al., 2016c). At high pH, the solubility of sulfide increases considerably, thus increasing the risk of inhibition of the biological activity (Mora et al., 2015).

$$H_2S_{(g)} \xrightarrow{H} H_2S_{(aq)} \xrightarrow{ka1} HS^-_{(aq)} + H^+ \xrightarrow{ka2} S^{2-}_{(aq)} + 2H^+ \quad (13)$$

$$m = \frac{[H_2S]_{(g)}}{[H_2S]_{(aq)} + [HS^-]_{(aq)} + [S^{2-}]_{(aq)}} = \frac{H}{1 + \frac{ka1}{10^{-pH}} + \frac{ka1 \bullet ka2}{10^{-2 \bullet pH}}} \quad (14)$$

The usual working pH range for an anoxic BTF ranges between 6.8 and 7.8 (Brito et al., 2017, 2018, 2019, 2020, 2019; Cano et al., 2019, 2021; Dupnock and Deshusses, 2020; Fernández et al., 2013, 2014). For this pH range, the dimensionless constant "m" is in the range of 0.32 to 0.07, i.e. the solubility is increased by 1.5- to 6.7-times. Working at acidic pH causes the inhibition of the growth of denitrifying bacteria due to the presence of free nitrous acid (NHO_2^-) (Zhou et al., 2011).

The geometry and flow mode affect the effectiveness of the anoxic BTF. Thus, a high H/D ratio increases the H_2S RE (Cano et al., 2019) and mass-transfer rate by improving the axial distribution of the liquid phase (Boyadjiev et al., 2016). However, the installation costs are higher due to the higher height and pressure drop (Lebrero et al., 2014). The BTFs described in the literature have an H/D ratio of between 1.7 (Almenglo et al., 2016a, 2016b) and 9.8 (Cano et al., 2019, 2021), except for the BTF described by Dupnock and Deshusses (2020), where H_2S was oxidized anoxically and CO_2 was reduced with H_2, which has an H/D ratio of 38.1. Therefore, a higher H/D ratio results in a lower TLV being required to achieve the EC_{MAX}. In addition, the recirculation flow rate will be lower for the same TLV. To date, anoxic BTFs have been operated and evaluated at TLVs of between 2.3 and 21 m h^{-1}. Operating at high TLVs can cause thickening of the liquid layer to levels that reduce the interfacial area and lead to a decrease in mass transfer (Jin et al., 2005).

On the other hand, low recirculation flow rates can lead to poor radial distribution and a higher proportion of stagnant liquid (Almenglo et al., 2016c), which in turn leads to a lower effective interfacial area and a poorer nitrate/nitrite supply to the biofilm. Fernández et al. (2013) observed a decrease in the RE below a certain TLV. These authors found that this optimal value depended on the IL, such that for ILs of 78.4 and 201 gS-H_2S m^{-3} h^{-1}, the optimal TLV was 15 m h^{-1}. Similar results were reported by Fernández et al. (2014) who found no discernible influence for TLV values higher than 13.7 m h^{-1} for ILs below 201 gS-H_2S m^{-3} h^{-1} working with OPUF. Almenglo et al. (2019) evaluated the effect of TLV, IL and nitrate concentration on removal efficiency using a response surface methodology. These authors observed that, when the nitrate concentration is not limiting, the effect of TLV on removal efficiency is only noticeable for ILs above 109.1 gS-H_2S m^{-3} h^{-1}. They hypothesized that the improvements observed may be due to an increase in the wetted area (Onda et al., 1968), an increase in the liquid retained on the support and an increase in the area in contact with the flowing liquid (Almenglo et al., 2016c). Similarly, Cano et al. (2019) evaluated the effect of TLV in both co-current and counter-current mode and observed an influence of TLV below 10 m h^{-1} in counter-current mode for an IL of 173.2 gS-H_2S m^{-3} h^{-1}. In contrast, when operating in co-current mode, the RE was not significantly affected when increasing the TLV above 5 m h^{-1}.

2.3. Others reactors

Other types of reactors with immobilized biomass have been used for the removal of H_2S from biogas under anoxic conditions. These include conventional biofilters (Jaber et al., 2017), fixed-film bioscrubbers (Bayrakdar et al., 2016; Pokorna et al., 2015), hollow fiber membrane bioreactor (HFMB) (Das et al., 2022) and horizontal fixed-bed reactors (Chinalia et al., 2012; de Bello Solcia Guerrero et al., 2020). Jaber et al. (2017) evaluated the use of two packing materials as support material in a biofilter. To maintain the moisture content of the media and provide nutrients, the bed was sprayed with a nutrient solution (5 min every hour). When expanded schist was used as packing material, the EC_{MAX} was 28.5 gS-H_2S m^{-3} h^{-1} (empty bed residence times (EBRT) = 300 s, 1100 ppm_v). In contrast, when the biofilter was packed with cellular concrete, it showed an EC_{MAX} of 23.7 gS-H_2S m^{-3} h^{-1} (EBRT = 240 s, 900 ppm_v). Bayrakdar et al. (2016) used a bioscrubber for the purification of real biogas from a manure digester on a laboratory scale. An upflow fixed bed reactor was used as anoxic bioreactor to obtain an H_2S RE of more than 95% in the scrubber. Pokorna et al. (2015) used a bioscrubber, with a downflow immersed biofilter with recirculation as an anoxic reactor. These systems operated stably up to an IL of 6.6 gS-H_2S m^{-3} h^{-1}. However, when operating at 16.6 gS-H_2S m^{-3} h^{-1}, the anoxic reactor lost efficiency (45%) and nitrite production increased. Zeng et al. (2018) used a biotrickling filter with a flooded part and packed it with Pall rings. These authors used synthetic wastewater and aerated anaerobic digester sludge as nitrate source, obtaining an average EC of 30.6 gS-H_2S m^{-3} h^{-1} in the former case and 22.42 gS-H_2S m^{-3} h^{-1} when using aerated sludge. The use of HFMB in biogas biodesulfurization has been recently published (Das et al., 2022). The high specific surface area and the lower probability of clogging make them very attractive. Das et al. (2022) used a submerged hollow fiber module of 0.0138 m^2 with an area-volume ratio of 2000 m^2 m^{-3} to simultaneously treat H_2S and NH_3 contained in the biogas (EC_{MAX} = 162 gS-H_2S m^{-3} h^{-1}). This technology is promising and open to future research in order to deepen its optimization, scaling and economic feasibility.

3. Suspended growth bioreactors

Although FBBs have been successfully applied to waste-gas treatment, some common operating problems have been widely reported in the literature. These include a loss of moisture, difficulty controlling the pH, lack of nutrients and clogging issues (Rene et al., 2012). The continuous operation of SGB could overcome some of these operational limitations because it offers a stable and completely mixed environment for bacteria. With the exemption of bioscrubbers, in general, SGBs are often overlooked when designing a biological treatment system for contaminated air streams. To maximize the mass transfer, the gas is normally introduced into the bottom of the bioreactor in the form of dispersed bubbles using diffusers. All the configurations reported so far are represented in Fig. 4.

The accumulation of sulfur can be slowed by operating at high fed N/S molar ratios, which promote the complete oxidation of sulfide to sulfate. Although sulfate production is undesirable as it can be reduced again to H_2S under anaerobic conditions by microbial agents such as sulfate reducing bacteria (Celis-García et al., 2008), in some cases sulfate production is promoted because it can be applied as fertilizer (Fontaine et al., 2021).

A possible solution to avoid the main drawbacks of BTF utilization for sulfur production would be the use of SGBs as the lack of a support to which elemental sulfur can adhere means that it can be recovered from the liquid medium. Furthermore, this elemental sulfur is generated as a stable colloidal suspension, thereby hindering its accumulation inside the bioreactor. This biogenic elemental sulfur can be sold as a feedstock in chemical industries or as a fertilizer, thus improving the overall economics of the bioprocess. Furthermore, several studies report the use of biogenic sulfur as a promising energy source for autotrophic denitrification of groundwater due to its better solubility compared to chemical sulfur (Ucar et al., 2021).

If elemental sulfur has to be isolated, the application of a separation step from the liquid phase is required due to its stability. Different physical and/or physicochemical methods can be used to separate the sulfur produced. The most popular methods include gravity sedimentation (Janssen et al., 1997), centrifugation (Cai et al., 2017), flotation (Liu et al., 2021), membrane separation (Camiloti et al., 2016), extraction (Ji et al., 2016) and coagulation-flocculation (Feng et al., 2018; Mora et al., 2020).

Several authors have tested different types of SGBs to achieve anoxic desulfurization while promoting elemental sulfur production. A brief compilation of the reports using different SGBs will be presented below.

3.1. Gas-lift bioreactors

Gas-lift bioreactors are pneumatically agitated bioreactors where the injection of a gas stream into one zone, the riser, causes the gas-liquid to be less dense than the rest of the liquid around it. This lower density makes this fluid be displaced upwards until it reaches the downcomer, an interconnected section by means of a draft tube that receives no gas. Gas-lift bioreactors are usually the preferred SGB in the field of waste-gas treatment (Fig. 4a) as they have some advantages over other SGBs, such as good transfer and energy efficiency, lack of moving mechanical parts and easier cleaning process (Zhang et al., 2016).

As is the case with the other SGBs described above, most reports include the use of gas-lift bioreactors for biological desulfurization using oxygen as an electron acceptor.

Some studies have also been conducted using gas-lift bioreactors under anoxic conditions. Thus, Q Mahmood et al. (2007) compared the sulfide oxidation (from a sulfide solution) of two different gas-lift bioreactors using nitrate and nitrite as electron acceptors and concluded that nitrite could be a better choice compared to nitrate due to the superior performance of the former. González-Cortés et al. (2020) have performed anoxic desulfurization in a gas-lift bioreactor fed with a biogas substitute stream containing H_2S. The main results of this work establish the gas-lift bioreactor as a very good alternative to BTF due to the high EC 177 gS-H_2S m^{-3} h^{-1} (RE = 98.1%) and high elemental sulfur selectivity (99%) obtained. Although this approach could save the costs of installing an absorption column, introducing the biogas from the bottom of the bioreactor would require the use of a blower, thus resulting in an increase in the operating costs of this technology that has to be taken into account.

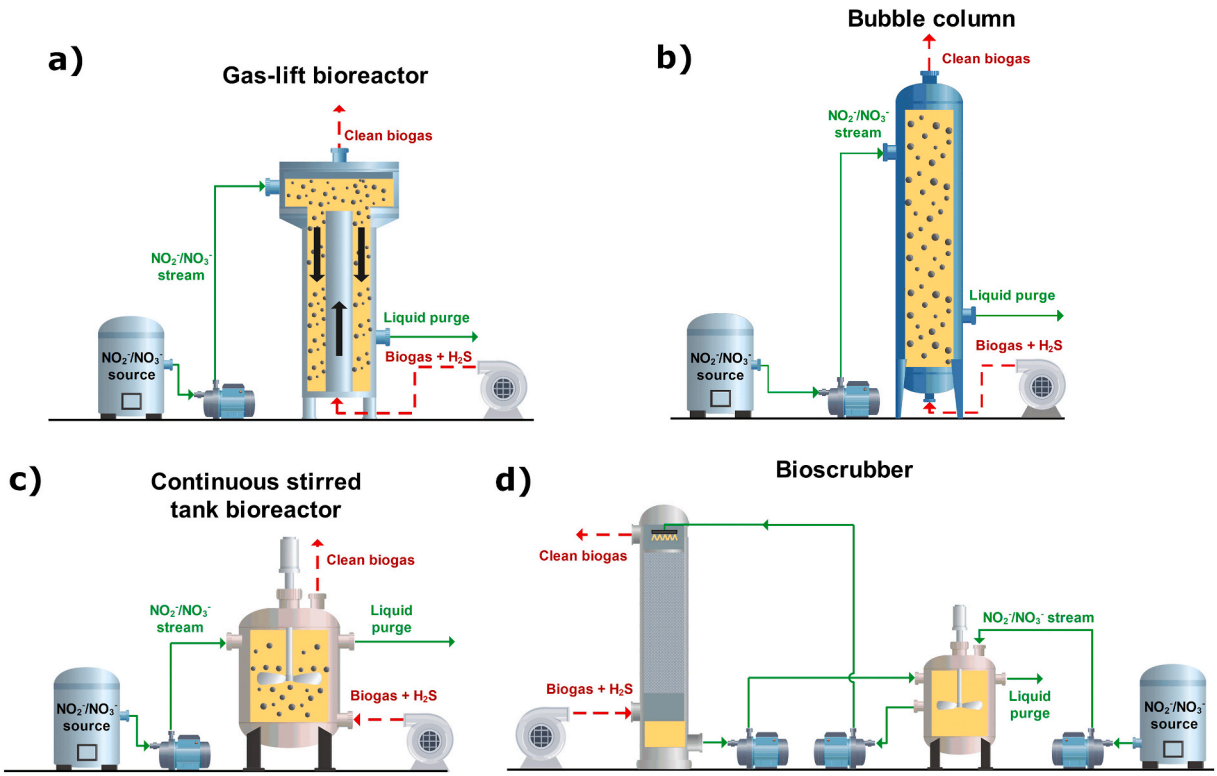

Fig. 4. Compilation of suspended growth bioreactors reported in the literature that have been used successfully for anoxic desulfurization.

3.2. Bubble column bioreactors

Like gas-lift bioreactors, bubble columns are bioreactors that do not need to be mechanically stirred as they use the entry of gas to both mix and aerate (Fig. 4b). These bioreactors consist of a cylindrical vessel where the gas is introduced at the base of the column through spargers. However, in these bioreactors, no additional liquid circulation is achieved in addition to that caused by the bubble flow. Due to their simplicity and low shear stress forces, bubble columns have been selected to study the anoxic desulfurization by some authors. Thus, Li et al. (2016) studied the influence of the fed N/S molar ratio on the H_2S RE using nitrate as electron acceptor and found that a decrease in the N/S molar ratio led to a reduction in the H_2S RE and reduced sulfate production, most likely favoring elemental sulfur production. Deng et al. (2009) also studied the anoxic desulfurization of biogas in a 3.9 L bubble column bioreactor with real biogas and using swine wastewater as a source of nitrogen. These authors studied the effect of adding different packing materials to enhance the RE of nitrate/nitrite and H_2S. Recently, Sempere et al. (2022) observed in two pilot bioreactors how low concentrations of nitrate (<10 mgN-NO_3^- L^{-1}) and alkalinity (<100 mg $CaCO_3$ L^{-1}) limited the H_2S removal.

Other authors studied the performance of a pilot-scale hybrid bubble column and scrubber tower (2.4 m^3, of which 1.2 m^3 was the liquid volume) (Baspinar et al., 2011; Turker et al., 2012). Baspinar et al. (2011) reported the highest EC_{MAX} in the literature (570 gS-H_2S m^{-3} h^{-1}; RE 87%) using an SGB. However, they reported an ECcrit of 166 gS m^{-3} h^{-1} (RE > 95%), similar to ECcrit valuesz reported by other authors such as González-Cortés et al. (2020) (177 gS m^{-3} h^{-1} (RE 99%)). Despite obtaining a high EC_{MAX}, the effluent generated in the process contained high nitrate and nitrite concentrations (up 200 mg NO_3^- L^{-1} and up 275 mg NO_2^- L^{-1}), requiring an additional treatment step. This reactor was continuously percolated with a liquid flow rate up to three-times the biogas flow rate from an aerobic activated sludge reactor for nitrogen removal.

3.3. Continuous stirred tank bioreactors

Continuous stirred tank bioreactors (CSTBRs) consist of cylindrical vessels mixed by mechanical stirrers resulting in completely mixed systems. Like other SGBs, the gas is injected under pressure through a sparger which generates bubbles that are broken down and dispersed by impellers creating a homogeneous environment. However, the shear stress introduced by the impellers which is directly related to the stirring speed is a disadvantage to be considered. Most of the research concerning H_2S removal in CSTBRs has been conducted using solutions of sulfide salt as feed (Can-Dogan et al., 2010; Dolejs et al., 2015). This methodology makes sense when the CSTBR is intended to remove sulfide from wastewater or to be studied as part of a bioscrubber in which the absorption column generates this liquid effluent rich in HS^-. However, the effect of interesting operational parameters, such as GRT or the effect of bioreactor configuration on the mass transfer of H_2S from biogas to the liquid, cannot be studied. Dolejs et al. (2015) followed this methodology in a CSTBR to achieve anoxic desulfurization, testing the effect of different fed N/S molar ratios on sulfide removal using nitrate as electron acceptor. They found that a reduction in the N/S molar ratio from 1.18 to 0.36 led to a decrease in sulfide RE from 96% to 55%. Despite obtaining high removal efficiencies, the sulfide ILs tested were quite low (less than 8 gS-H_2S m^{-3} h^{-1}). The accumulation of sulfur as a colloidal suspension was also found. Higher sulfide ILs were tested by Can-Dogan et al. (2010), who found that REs remained above 92% for hydraulic residence times (HRTs) ranging from 86.4 to 2 h.

González-Cortés et al. (2021b) also studied anoxic desulfurization in a CSTBR using a biogas mimic with H_2S to feed the system and nitrite as electron acceptor (Fig. 4c), subsequently optimizing the main operational parameters such as GRT, HRT or stirring speed. One of the most important findings of this study was the sensitivity of the nitrite-reducing sulfide-oxidizing bacteria to shear-stress forces. In addition, a significantly high maximum EC of 166.0 ± 7.2 gS-H_2S m^{-3} h^{-1} (RE = 71.7%) was obtained at a GRT of 41 s.

3.4. Bioscrubbers

The bioscrubbers used for waste gas treatment comprise two units: (i) an absorption column (filled with a packed bed or empty), and (ii) a biological treatment bioreactor, usually a stirred bioreactor (Fig. 4d). The use of this technology to remove H_2S from biogas has been widely reported in the literature. However, most reports use oxygen as electron acceptor for the biological removal of HS^- (Roosta et al., 2012; San--Valero et al., 2019).

The use of bioscrubbers to perform the anoxic desulfurization of biogas and produce elemental sulfur has been reported recently (Flores-Cortés et al., 2021; Quijano et al., 2021). Thus, Flores-Cortés et al. (2021) obtained removal efficiencies higher than 95% for H_2S ILs ranging from 16.2 to 51.9 gS-H_2S m^{-3} h^{-1}. During the whole operation, elemental sulfur was obtained as the main oxidation product and was successfully removed, thereby avoiding clogging issues. A similar experimental configuration was used by Quijano et al. (2021) who studied the impact of anoxic desulfurization on the CH_4 and CO_2 content of the biogas stream. An EC_{MAX} of 35.7 ± 2.0 gS-H_2S m^{-3} h^{-1} was obtained in that study.

Table 2
Main advantages and drawbacks of the different configurations used to perform the anoxic H_2S abatement in biogas.

	TECHNOLOGY	ADVANTAGES	DRAWBACKS
FIXED-BIOMASS BIOREACTOR	BIOTRICKLING FILTER	- Simple and compact design. - High biomass concentration. - High H_2S elimination capacity. - Low pressure drop - Low energy consumption. - Easy control of temperature, pH and nutrients. - Operational stability. - Durability of the packing materials.	-More complex in operation and higher operating and capital costs compared to biofilters. - Risk of clogging (biomass and S^0 accumulation). - No sulfur recovery. - Production of a waste stream.
	BIOFILTER	- Simple design. - Low capital and operating costs. - Easy operation and maintenance. - High removal efficiencies. - Low pressure drop. - Low water consumption - No generation of waste streams	- Useful only for low inlet loads. - Packing material compaction - Risk of clogging (biomass and S^0 accumulation). - Difficult control of temperature, pH and nutrients. - No sulfur recovery.
	FIXED-FILM BIOSCRUBBER	- High biomass concentration. - High H_2S elimination capacity. - Low pressure drop. - Easy control of temperature, pH and nutrients. - Operational stability.	- Relatively complex design - Relatively complex operation and maintenance. - Production of a waste stream. - No sulfur recovery.
	HOLLOW FIBER MEMBRANE BIOREACTOR	- High specific surface area. - Low probability of clogging in the gas phase. - High H_2S elimination capacity. - Easy control of temperature, pH and nutrients. - No moving parts	- High capital costs. - Long-time operation can lead to clogging in the liquid phase. - Complex scaling-up design. - Production of a waste stream.
	HORIZONTAL FIXED-BED REACTORS	- High biomass concentration. - Easy control of temperature, pH and nutrients. - Operational stability. - Durability of the packing materials.	- High pressure drop. - More complex operation and higher operating costs compared to biotrickling filters. - No sulfur recovery. - Production of a waste stream.
SUSPENDED GROWTH BIOREACTORS	GAS-LIFT BIOREACTORS	- High H_2S elimination capacity. - Low energy consumption. - Lack of moving mechanical parts. - Easier cleaning process. - Allows sulfur recovery. - Temperature, pH and nutrient control. - Low shear stress forces	- Low biomass concentration. - High pressure drop. - Production of a waste stream. - Biomass is more sensitive to high H_2S concentrations in biogas.
	BUBBLE COLUMNS BIOREACTORS	- Simple design. - Low shear stress forces. - Does not require mechanical stirring. - Easy control of temperature, pH and nutrients. - Allows sulfur recovery.	- Low biomass concentration. - High pressure drop. - Production of a waste stream. - Biomass is more sensitive to high H_2S concentrations in biogas.
	CONTINUOUS STIRRED TANK BIOREACTORS	- High H_2S elimination capacity. - Easy control of temperature, pH and nutrients. - Allows sulfur recovery.	- Low biomass concentration. - High pressure drop. - Requires mechanical stirring. - Relatively high shear stress forces. - Production of a waste stream. - Biomass is more sensitive to high H_2S concentrations in biogas.
	BIOSCRUBBERS	- High H_2S elimination capacity. - Low pressure drop. - Easy control of temperature, pH and nutrients. - Allows sulfur recovery. - Deals better with peaks in the inlet concentration.	- Relatively complex design - Relatively complex operation and maintenance. - Production of a waste stream. - Biomass is more sensitive to high H_2S concentrations in biogas.

A pilot-scale anoxic bioscrubber has been constructed with funding from the ongoing LIFE biogasnet project in a landfill to desulfurize real biogas (Gamisans et al., 2021; Torres-Herrera et al., 2022a, 2022b). The prototype consists of a nitrification sequencing batch bioreactor (SBR) with a capacity of 1 m^3 that is used to treat landfill leachate (used as a nitrogen source for nitrite/nitrate production) and an anoxic bioscrubber comprising a 1 m^3 CSTBR and an absorption column with a packed volume of 0.19 m^3. The average biogas flow rate was of 43.0 ± 12.2 m^3 h^{-1} with an operation time of 38 weeks. The best results were obtained with a biogas flow rate of 55 m^3 h^{-1} (inlet concentration 109 ± 5.8 ppm_V) with an outlet H_2S concentration of 3.0 ± 1.2 ppm_V (RE 97.1 ± 1.1%; EC = 9.6 ± 0.5 g$S\text{-}H_2S$ m^{-3} h^{-1}) (Torres-Herrera et al., 2022b). A total leachate volume of 8929 L was nitrified (ammonium concentration of 1410 ± 362 mg $N\text{–}NH_4^+$ L^{-1}), being nitrate the main oxidation product, with a mass flow production between 61 and 84 g $N\text{–}NO_3^-$ d^{-1} (Torres-Herrera et al., 2022a).

The use of this configuration would require the construction of an absorption column where the gas-liquid mass transfer happens. These towers are design to operate with low pressure drop, so the inlet gas, which is normally found at atmospheric pressure, can be directly injected into the absorption column. In contrast, the other SGBs requires mandatorily the use of a blower to inject the gas from the bottom of the bioreactor.

The main advantages and drawbacks of the different configurations tested to perform the anoxic biogas biodesulfurization are summarized in Table 2. Among all the configurations, BTFs have demonstrated the capacity to deal with high H_2S ILs using a compact and relatively simple design which has been shown in many studies to be stable in long-term operations. Its major disadvantage is the risk of clogging caused by the accumulation of S^0 and biomass, although certain strategies have been proposed to reduce this problem. The number of papers published using other FBBs is significantly lower, of which HFMB constitutes the most promising technology. Although moderate to high ECs have been achieved, further studies are required to verify their performance in long-term operations and elucidate possible scaling-up problems and associated costs. In contrast, SGBs have a lower biomass concentration, which affects the biological capacity to degrade H_2S. Although they can achieve mass transfer coefficients similar to those of BTFs, the ECs of this type of reactor are generally lower compared to the ones of the BTFs. Therefore, using SGBs would require a larger reactor volume and a gas blower to overcome the water column pressure. It is also important to note the susceptibility of sulfur-oxidizing bacteria to shear stresses, which limits the stirring speed in the SGBs where mechanical stirring occurs. A different case is that of bioscrubbers, where a high EC can be achieved in the absorption tower avoiding the operation costs of a blower overcoming the water column pressure. However, the volume of the biological reactor will be higher, mainly dependant on the concentration of microorganisms, much lower than the present in FBBs.

4. Integrated systems

One of the main drawbacks of anoxic desulfurization of biogas is the increase in operational expenditures (OPEX) and the environmental impact if commercial nitrate or nitrite is used (Cano et al., 2018). Thus, OPEX costs can increase from 1.71 to 2.47 € per one hundred cubic meter of biogas treated if commercial nitrate is employed compared to the scenario with a nitrified effluent. Furthermore, a life cycle assessment (LCA) showed an increase of up to 61.4% in the impact category of climate change if commercial nitrate is used as electron acceptor source instead of the effluent from a nitrification bioreactor. In this way, using an already nitrified effluent to desulfurize biogas, only 7.2 kg CO_2 equivalent per kg of $S\text{–}H_2S$ treated is emitted, compared to 25.3 kg CO_2 equivalent when using chemical nitrate (Cano et al., 2018). In any case, the environmental impact is much lower using biological technologies compared to conventional technologies such as chemical scrubbers (30 kg CO_2 equivalent) or impregnated activated carbon (42.1 kg CO_2 equivalent).

As such, the use of nitrified effluent from an ammonium-rich source is clearly a good solution for the industrial application of this technology. In addition, two effluents can be treated simultaneously by integrating the nitrification of ammonium-rich effluents with anoxic biogas desulfurization. Although the percentage of ammonium-rich effluent nitrified will probably not be 100% of the effluent available at the site, the treatment of a fraction of it will always be an advantage. Nitrification of the ammonium-rich effluent can be full and/or partial since the use of nitrate and nitrite, separated or mixed is feasible (Brito et al., 2018). A further advantage of anoxic systems in terms of design is the easy control of oxidation selectivity since a linear relationship between the nitrogen (nitrate/nitrite) supplied and the sulfur/sulfate selectivity is obtained (López et al., 2018). A good approximation is provided by kinetic equations (2)–(7) or by the experimental linear regressions (eqs. (9)–(12)) (Almenglo et al., 2016a; Brito et al., 2018; Fernández et al., 2013; López et al., 2018). It is therefore not too challenging to determine the size of the nitrification unit depending on the desired product (sulfate or elemental sulfur) in the anoxic desulfurization system. It is worth noting that the use of nitrite will involve a higher volume of treatment for the ammonium-rich effluent as the nitrogen demand for H_2S oxidation is 1.6-times higher than for the use of nitrate (González-Cortés et al., 2021a). As such, partial nitrification to nitrite may be desirable in the case of high availability of ammonia or ammonium rich liquid or gas streams such as exhaust air from intensive pig production (Liu et al., 2017). Moreover, partial nitrification has lower aeration requirements and therefore lower OPEX, although control of the partial nitrification system can be more complex (Capodici et al., 2019; Sri Shalini and Joseph, 2012). In the denitrification process, an organic carbon source is normally used as electron donor. In the present technology, the H_2S contained in the biogas stream is used to reduce the nitrate/nitrite produced in the nitrification stage, thereby removing the need for an organic carbon source.

One of the pioneering studies in this area, in which nitrified wastewater from an SBR was used to feed a BTF, was carried out by Soreanu et al. (2008c). However, these authors supplemented the SBR effluent with nitrate (up to 0.6 g$N\text{-}NO_3^-$ L^{-1}). Although a good H_2S RE (99%) was obtained, the EC was 4.85 g$S\text{-}H_2S$ m^{-3} h^{-1}. Since 2008, the number of research articles dealing with anoxic biogas desulfurization processes has increased, although the use of biological nitrate/nitrite sources remains scarce. Furthermore, there are very few studies involving both nitrification and desulfurization bioreactors, and in some cases, only the nitrified effluent from the other system is used, sometimes even with nitrate supplementation, which is not the most desirable option. One of the most important variables in these systems is the nitrate/nitrite mass flow rate fed to the anoxic system, as this affects the N:S ratio and, therefore, the oxidation products selectivity (Cano et al., 2021; González-Cortés et al., 2021a). On the other hand, the use of an intermediate tank is required to store the nitrified medium in systems with batch nitrification processes such as SBR (Gamisans et al., 2021). It has been shown that simple sedimentation of the nitrified medium is sufficient to obtain an effluent that can be used in the anoxic system (Cano et al., 2019; González-Cortés et al., 2021a), although it is also possible to use sand filters (Zeng et al., 2019). Other systems use a nitrification bioreactor with immobilized biomass and feed the nitrified effluent directly into the anoxic system. In this case, we can find systems with nitrification and desulfurization in the same equipment (de Bello Solcia Guerrero et al., 2020; Pantoja Filho et al., 2015) or separate ones (Chinalia et al., 2012; de Bello Solcia Guerrero et al., 2020).

Some examples of ammonium-rich effluents used include swine wastewater (Deng et al., 2009; Wang et al., 2015), slurry from a rural household anaerobic digester (Zeng et al., 2019), domestic sewage from a primary sedimentation tank in a WWTP (Xu et al., 2020) and landfill leachate (Gamisans et al., 2021; González-Cortés et al., 2021a). Deng et al. (2009) used intermittent aeration to nitrify the digested effluent from the anaerobic digester. The nitrified effluent was decanted and the

ranges of N–NH_4^+, N–NO_2^- and N–NO_3^- were between 4 and 12, 2–65 and 24–117 mg N L^{-1}, respectively. On the contrary, the swine slurry nitrified in the study carried out by Wang et al. (2015) contained a nitrate concentration between 24 and 91 mg L^{-1} and almost no nitrite or ammonium. Baspinar et al. (2011) used wastewater from four aeration ponds in series. The ammonium concentration in the nitrified effluent was kept very low, instead nitrite (100–375 mg L^{-1}) and nitrate (50–300 mg L^{-1}) concentrations were appreciable. Zeng et al. (2019) obtained after the aeration an effluent with the following concentration ranges: 150–250 mg N–NH_4^+ L^{-1}, 4.4–177.1 mg N–NO_2^- L^{-1} and 3.2–302.3 mg N–NO_3^- L^{-1}. González-Cortés et al. (2021a) treated landfill leachate (1997 mg N–NH_4^+ L^{-1}) and the average nitrate and nitrite concentrations were of 363 ± 119 and 80 ± 58 mg N L^{-1}, respectively. Therefore, a wide variety of nitrified effluents are susceptible to being used in the anoxic bioreactor. Other interesting effluent is pig slurry, because in pig farms biogas can be produced (Hollas et al., 2022) and pig slurry can be nitrified (Burton, 1992). However, this scenario has not been studied yet. With regard to the desulfurization unit, several types of bioreactors can be found in the literature, including bubble columns with and without packing material (Deng et al., 2009; Sempere et al., 2022; Wang et al., 2015), bioscrubbers (Baspinar et al., 2011; Gamisans et al., 2021; Turker et al., 2012), BTFs (Cano et al., 2018, 2021; Pantoja Filho et al., 2015; Tanikawa et al., 2018; Zeng et al., 2019), gas-lift bioreactors (González-Cortés et al., 2021a), horizontal-flow bed-packed reactors (Chinalia et al., 2012; de Bello Solcia Guerrero et al., 2020) and expanded granular sludge beds (Xu et al., 2020).

In FBBs, it is common to try to obtain complete H_2S oxidation to sulfate, in order to avoid clogging of the packed bed by elemental sulfur. For example, Cano et al. (2021) obtained 98.3% sulfate selectivity in a BTF with a fed N:S ratio of 1.6 mol mol^{-1}. However, most anoxic bioreactors are operated at N:S ratios of less than 1 mol mol^{-1} (Deng et al., 2009; Xu et al., 2020), therefore the formation of some sulfur is unavoidable.

In most cases, sulfur-oxidizing bacteria (SOB) produce extracellular elemental sulfur globules, forming colloidal particles with a size up to 1 μm, which in turn form aggregates, thus favoring immobilization (Janssen et al., 1999). As such, it is advisable to use a low initial N:S ratio.

As stated in Section 3, the sulfur produced in SGBs can be recovered for valorization. Indeed, both elemental sulfur and sulfate could have applications as fertilizers (Fontaine et al., 2021). However, there are no published studies about the use of oxidation products as fertilizer, and even quality characterization of the elemental sulfur produced (biomass concentration, metal content, etc.) has received little attention (Fan et al., 2022; Mol et al., 2020). Therefore, depending on the final oxidation product targeted, one type of bioreactor or another will be more suitable. Thus, whereas the use of FBBs, in which a better mass transfer, and therefore a better removal efficiency, can be achieved, is recommended if sulfate is desired, SGBs are the best option if the production of elemental sulfur is preferred. The highest ECs obtained using integrated systems with a fixed-biomass anoxic bioreactor include those reported by Zeng et al. (2019), with an EC_{MAX} of 76.5 gS-H_2S m^{-3} h^{-1} (RE 94.5%), and Cano et al. (2021), with an EC_{MAX} of 151.9 gS-H_2S m^{-3} h^{-1} (RE 97.3%). For SGBs, the highest EC was obtained by González-Cortés et al. (2021a), who used a gas-lift bioreactor and achieved a value of 141.18 gS-H_2S m^{-3} h^{-1} (RE 95%, GRT 41 s). Furthermore, it appears that the use of gas-lift bioreactors, which have a good mass transfer and are suitable for shear-sensitive microorganisms (Guieysse et al., 2011), enhances elemental sulfur production, with values of up to 95% being reported (González-Cortés et al., 2021a).

Deng et al. (2009) used much higher GRTs of between 1.1 and 15.76 min, with bubble columns and an RE of more than 90%, and found a better performance when packing material was added, as mentioned in section 2.4. A similar EBRT of 15 min has been used by Baspinar et al. (2011) with a bioscrubber, but in this case treating biogas with an inlet H_2S concentration of up to 3.65% (36,500 ppm_v). As stated in section 3.3, in this case, the H_2S RE was 87% with an EC_{MAX} of 570 gS-H_2S m^{-3} h^{-1}.

In studies with horizontal-flow bed-packed reactors, the maximum ILs reported to date are 33.2 (RE 94.1%) (Chinalia et al., 2012) and 29.1 gH_2S m^{-3} h^{-1} (RE 64.3%) (de Bello Solcia Guerrero et al., 2020). Lower ILs can be treated using organic media in biofilters such as coconut chips. For example, Tanikawa et al. (2018) achieved an H_2S RE of 99% for an IL of 5.57 gH_2S m^{-3} h^{-1}. de Bello Solcia Guerrero et al. (2020) compared two different FBB configurations for biogas desulfurization coupled with nitrogen removal. The first reactor in both cases was a horizontal aerobic reactor, in which a nitrification process was carried out. In the first configuration, the anoxic reactor was a horizontal fixed-bed reactor, which allowed the authors to obtain an EC_{MAX} of 18.7 gS-H_2S m^{-3} h^{-1}. The second configuration had a vertical fixed-bed reactor, in which the gas and liquid flows rise in co-current, as an anoxic reactor, and with this system they obtained an EC_{MAX} of 10.2 gS-H_2S m^{-3} h^{-1}. Chinalia et al. (2012) used two pilot-scale horizontal reactors for simultaneous removal of H_2S and nitrogen. The first reactor (aerobic) was responsible for nitrate production and the second reactor was used for anoxic desulfurization of biogas, achieving an EC_{CRIT} of 31.25 gS-H_2S m^{-3} h^{-1} (RE > 99%, 20,000 ppm_v and EBRT = 21.2 min). As regards nitrogen removal, the ammonium removal efficiency was higher than 90% in all the above cases, with nitrate being the main oxidation product. As has been shown, all previous studies are successful, despite different configurations in the anoxic stage and diversity of nitrified effluents, demonstrating the robustness of simultaneous biogas desulfurization and nitrogen removal.

5. Microbial communities

The performance and effectiveness of the anoxic desulfurization of biogas are dependent on the microbial communities concerned. Therefore, it is essential to determine the composition and resilience of these microbial communities in different environments when exposed to different operating conditions to allow potential improvements to be proposed to increase the removal efficiency of the bioreactor. In this section, SOBs are briefly presented as being mainly responsible for the oxidation of reduced sulfur compounds in the sulfur cycle context. Subsequently, a compilation of the molecular techniques used to characterize the bacterial communities present in anoxic BTFs and SGBs, and their results, are described.

H_2S is not toxic for these bacteria, the so-called chemolithotrophic SOB, which mainly explains why bioreactors are able to remove this compound from biogas. These bacteria are well-known to be able to grow under a broad range of pH and temperature conditions, to resist high concentrations of sulfide and to have low nutrient requirements (Le Borgne and Baquerizo, 2019). Despite most SOBs being aerobic, some species of *Thiobacillus*, *Sulfurimonas* and *Thioalkalivibrio*, amongst others have been reported to be capable of using NO_3^- and NO_2^- as electron acceptors (Shao et al., 2010). These compounds are subsequently reduced to nitric oxide (NO), nitrous oxide (N_2O) and nitrogen gas (N_2) in a process known as autotrophic denitrification when using CO_2 as carbon source.

When considering the analysis of microbial communities present in the bioreactors, it is fundamental to note that biofilm conditions are not easily reproducible. This, coupled with the difficulty of culturing anoxic chemolithotrophic SOBs, makes its determination using the classic microbiological methods complex (Le Borgne and Baquerizo, 2019).

A brief summary of studies characterizing the microbial consortia present in bioreactors used for anoxic desulfurization can be found in Table 3. Although most of these analyses are performed in BTFs, bacterial identification of the biomass present in SGBs has been published recently.

The first study to attempt to characterize the microbial composition of a bioreactor used for anoxic desulfurization was published by Fernández et al. (2013). Samples from the top, bottom and recirculation

Table 3
Overview of studies analyzing the microbial composition of bioreactors used for the anoxic desulfurization of biogas.

Bioreactor	Electron acceptor	Inlet gas	EC_{MAX} ($gS\text{-}H_2S\ m^{-3}\ h^{-1}$)	Packing material	Inoculum	Molecular technique	Main results	Ref.
BTF	NO_3^-	Biogas from UASB bioreactor	170	Polypropylene pall rings	Biomass from OPUF cubes of previous BTF	DGGE	Same bacterial populations throughout the packed bed	Fernández et al. (2013)
BTF (pilot-scale)	NO_3^-	Biogas from anaerobic digester	140	OPUF cubes	Activated sludge from a municipal wastewater treatment plant	Amplicon pyrosequencing	*Sedimenticola* was the main SOB The flow pattern affects bacterial diversity Significant presence of heterotrophic denitrifiers	Almenglo et al. (2016a)
BTF	NO_3^-	Biogas from UASB bioreactor	–	OPUF cubes Polypropylene pall rings	Biomass from OPUF cubes of previous BTF	DGGE and identification of excised bands by ABI 3730 L capillary DNA sequencer	The bacterial community does not depend on the packing material (OPUF or Pall rings) *Thiobacillus* genus is predominant Presence of auxotrophic and heterotrophic bacteria with no sulfur-oxidizing capacity	Valle et al. (2018)
BTF	NO_3^-/ NO_2^-	Biogas mimic (N_2 and H_2S)	134	Polypropylene Pall rings	N.D.	DGGE	Reduction of microbial diversity after long term progressive replacement of NO_3^- by NO_2^-	Brito et al. (2018)
BTF[a]	NO_3^-/ NO_2^-	Biogas from anaerobic digester	25	Pall rings	Mixture of an aerobic activated sludge from a WWTP and anaerobic digestion slurry	NGS	IL greatly affects the microbial community structure *Thiobacillus* was the dominant genus under all conditions, followed by *Sulfurimonas*	Zeng et al. (2018)
BTF	NO_3^-/ NO_2^-	Biogas mimic (N_2 and H_2S)	19	Polyurethane foam	Biofilm from a *Thiobacillus* dominated moving bed biofilm reactor	DGGE	Operation of the BTF under mixotrophic conditions led to the development of heterotrophic denitrifiers competing for NO_3^- as electron acceptor with SOB	Khanongnuch et al. (2019c)
BTF[a]	NO_3^-/ NO_2^-	Biogas from rural household biogas plant	81	Polyurethane foam Multi-surface hollow spheres	N.D.	PE250 sequencing using Illumina Hiseq Rapid SBS Kit V2 (FC-402-4023,500 Cycle)	The microbial community was more stable below the liquid than above it. *Sulfurimonas*, *Rhodanobacter*, *Truepera* and *Thiobacillus* were the predominant genera during all stages	Zeng et al. (2019)
Gas-lift	NO_3^-	Biogas mimic (N_2 and H_2S)	141	N.A	Previous BTF	lllumina MiSeq platform	*Sulfurimonas* was the most common genus in the anoxic bioreactor, followed by *Thauera* and *Lentimicrobium*	González-Cortés et al. (2021a)
Bioscrubber	NO_3^-	Biogas mimic (N_2 and H_2S)	51	N.A	Secondary activated sludge from a municipal wastewater treatment plant	Illumina MiSeq sequencing analysis	*Sulfurimonas*, *Idiomarina* and *Stenotrophomonas* were the predominant genera during operation of the system	Flores-Cortés et al. (2021)

[a] Biotrickling filter with a flooded part.

taken from a lab-scale BTF fed with real biogas were analyzed by DGGE, with no significant differences being found between them. Subsequently, Valle et al. (2018) analyzed samples from two similar bioreactors operating under similar conditions but filled with OPUF cubes and Pall rings. The differences between both bioreactors were non-significant, thus highlighting the limited influence of the packing material on microbial diversity. The *Thiobacillus* genus was predominant in both bioreactors and the presence of auxotrophic and heterotrophic bacteria was observed. Almenglo et al. (2016a) operated a pilot-scale BTF fed with real biogas under different gas-liquid flow patterns and evaluated the bacterial composition under these different conditions by pyrosequencing of the tag-encoded FLX amplicon. *Sedimenticola* was found to be the main SOB (49.5%), whereas the presence of heterotrophic bacteria was significant. Brito et al. (2018) studied the effect of a progressive replacement of NO_3^- by NO_2^- in a lab-scale BTF fed with a biogas mimic on the microbial consortium. Although their results showed that the change in electron acceptor led to a reduction in microbial diversity, this reduction was reversible if NO_3^- was fed again. Khanongnuch et al. (2019c) operated a lab-scale BTF under mixotrophic conditions. A DGGE analysis of several samples under different operational conditions (different liquid flow rates, H_2S shock loads and wet-dry operations), showed only minimal differences. The mixotrophic conditions caused the growth of heterotrophic denitrifiers, which compete for NO_3^- as electron acceptor with the SOB. Zeng et al. (2018) operated an anoxic BTF with a flooded part fed with real biogas and two different effluents as nitrite/nitrate source, namely synthetic wastewater and a nitrified biogas slurry. The main genera found upon feeding of both effluents were *Thiobacillus* and *Sulfurimonas*, which accounted for >60% of the microbial communities. Furthermore, a significant influence of the H_2S IL on the microbial community structure was established. A similar set-up was operated by Zeng et al. (2019), who found *Sulfurimonas*, *Rhodanobacter*, *Truepera* and *Thiobacillus* to be the most predominant genera, accounting for 32–70% of the microbial consortium. These authors concluded that microbial diversity was more

stable in the flooded part of the BTF than above it.

This latter finding agrees well with those of González-Cortés et al. (2021a), who studied the microbial composition of an integrated system comprising a nitrification bioreactor (firstly fed with synthetic medium and secondly with landfill leachate) and an anoxic gas-lift bioreactor. These authors found a surprising predominance of the *Sulfurimonas* genus in the anoxic bioreactor, with a relative abundance of 91.8% when the synthetic medium was fed into the integrated system. It appears that the high ILs applied to this bioreactor, coupled with the stable liquid environment, led to a strong selective pressure that cannot be emulated in BTFs. The prevalence of this genus was reduced to 50.9% in favor of the genera *Thauera* (24.2%) and *Lentimicrobium* (9.7%) when nitrified landfill leachate was used as nitrate/nitrite source. Recently, Flores-Cortés et al. (2021) used an anoxic bioscrubber to desulfurize a biogas mimic. Again, *Sulfurimonas* was the predominant genus in the stirred tank (up to 50.1%), followed by *Stenotrophomonas*, *Myroides* and *Idiomarina*.

In conclusion, it can be considered that, of the huge diversity of operational taxonomic units (OTUs) found in the different bioreactors used for anoxic desulfurization, the genera *Thiobacillus*, *Sulfurimonas* and *Sedimenticola* play a key role in the removal of H_2S. Despite the different operational and environmental conditions tested, their presence seems to be related to the good performance of the different bioreactors. Despite all the data obtained to date, the number of studies concerning a microbial community analysis of pilot-scale bioreactors or bioreactors using real biogas instead of a biogas mimic remains scarce. As such, future research studies addressing this gap are required.

6. Conclusions and future directions

The use of biogas requires a desulfurization stage in order to avoid SO_2 emissions during its combustion and malfunctions in the valorization technology. In this regard, biological technologies are a serious competitor to conventional physicochemical technologies given their lower operational costs and environmental impact. Biological anoxic desulfurization is a young technology with a promising future given its advantages over aerobic biotechnologies (no biogas dilution, no risk of explosion and simultaneous treatment of two effluents).

In view of the results published to date, the main conclusion is the robustness of simultaneous biogas desulfurization and nitrogen removal given that all ammonium-rich effluents and bioreactor configurations studied are feasible. It will therefore be necessary to study each scenario to determine which configuration is the most suitable depending on the characteristics of the biogas, maximum outlet H_2S concentration allowed and characteristics of the ammonium-rich effluent. Consequently, more laboratory-scale studies are needed to determine the application ranges of each system according to the above-mentioned parameters. Moreover, it will also be essential to increase the number of pilot-scale studies and to set up demonstration or industrial scale plants, which will allow an accurate assessment of operational costs, installation costs and environmental impacts. The collaboration of all stakeholders will be essential to ensure the publication and dissemination of the results obtained, especially given that the experimental results obtained at full-scale are not usually published, thus making dissemination of the technology difficult.

Furthermore, ammonium-rich effluents are not homogeneous throughout the year, so long-term operation is essential to assess their effect on the nitrification and desulfurization stages. The configuration of control systems for stable operation and minimization of external disturbances will also be critical.

From a basic research point of view, it is a challenge to relate the microbial composition to the bioreactor operation. Indeed, although many OTUs can be found, the role of many of them is still unknown, and many others are as-yet unidentified. In any case, *Sulfurimonas* and *Thiobacillus* seem to be present in almost all systems. In FBBs, CFD modeling and the use of microsensors in the biofilm will allow an improvement of the mathematical models and performance of the systems.

With regard to the oxidation products (elemental sulfur and sulfate), it is mostly suggested that they can be used as fertilizer. As such, it will be necessary to perform field studies with these effluents or to look for alternative means of valorization.

To conclude, while from a scientific point of view anoxic desulfurization is a research field in which further progress can be made, from an application point of view the technology readiness level (TRL) is 6–7 (validation/demonstration in relevant environment), although there are still very few studies at this level of maturity. In any case, there is no doubt that TRL 8–9 (system complete and qualified – actual system proven in operational environment) will soon be achieved in some configurations for the simultaneous desulfurization and nitrification of ammonium-rich effluents.

Declaration of competing interest

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

Data availability

No data was used for the research described in the article.

Acknowledgments

This work has been co-financed by the European Union under the 2014–2020 ERDF Operational Programme and by the Department of Economic Transformation, Industry, Knowledge, and Universities of the Regional Government of Andalusia. Project reference: FEDER-UCA18-106138.

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