Removal of hydrogen sulfide from gas streams using biological processes - A review

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Syed, M., Soreanu, G., Falletta, P. and Béland M. 2006. **Removal of hydrogen sulfide from gas streams using biological processes - A review**. Canadian Biosystems Engineering/Le génie des biosystèmes au Canada **48**: 2.1 - 2.14. Hydrogen sulfide (H_2S) is a toxic and odorous compound present in biogas produced by the anaerobic digestion of biosolids and other organic materials. Due to its corrosive nature in internal combustion engines, biological hydrogen sulfide removal processes are being investigated to overcome the chemical and disposal costs associated with existing chemically-based removal processes. Both phototrophic and chemotrophic bacteria are suitable candidate microorganisms for hydrogen sulfide bioxidation. Phototrophic *C. limicola* is an ideal bacterium in these biological removal processes due to its ability to grow under anaerobic conditions using only inorganic substrates and a light source and its efficient extracellular production of elemental sulfur from H_2S. Phototrophic fixed-film reactors are an interesting concept for cost-effective H_2S removal from biogas due to their ability to operate for long periods of time without requiring a biomass separation step and their ability to operate under higher and variable loadings. However, a light source is one of the key constraints for this process. Chemotrophic bacteria can also be used in fixed-film reactors to produce elemental sulfur instead of sulfate under controlled oxygen conditions. These bioscrubbers are gaining acceptance for treating hydrogen sulfide containing gases from a wide variety of sources such as biogas, off-gases from wastewater treatment plants, livestock farms, etc. The biofilter medium is inexpensive and may contain sufficient micro-nutrients for the microbial communities. Future research needs include the optimization of the anaerobic biofiltration process, the development of a system combining the advantages of phototrophic and chemotrophic bacteria and the possible co-removal of siloxanes within this process. **Keywords:** hydrogen sulfide, phototrophic, chemotrophic, biological oxidation, biofiltration, bioscrubbing.

Le sulfure d'hydrogène (H_2S) est un composé toxique et odorant présent dans le biogaz produit par la digestion anaérobique des biosolides et de autres matières organiques. Ce composé peut causer la corrosion précoce des moteurs à combustion interne qui brule le biogaz pour générer de l'énergie. Récemment, certains procédés biologiques sont visés pour surmonter les coûts élevés relié aux processus chimiques d'élimination du sulfure d'hydrogène (coûts des produits chimiques et de l'élimination des déchets). Les microorganismes responsables pour la bio-oxydation du H_2S peuvent être de nature phototrophique ou chimiotrophique. Due à sa capacité de croissance rapide et de sa production extracellulaire du soufre élémentaire en utilisant seulement des substrats inorganiques en milieu anaérobique, la bactérie phototrophique *C. limicola* est suggérée. Les réacteurs à biomasse phototrophique fixée sont intéressants pour la conversion du H_2S grâce à leur facilité de séparer le soufre du biogaz et de leur capacité élevée d'opérer sous des charges et des conditions variables. Cependant, l'alimentation en énergie lumineuse est l'une des contraintes principales pour l'avancement de ce procédé avec la bactérie *C. limicola.* Les bactéries chimiotrophiques peuvent aussi être utilisées dans les réacteurs à biomasse fixée si l'on pratique un contrôle rigoureux de l'apport d'oxygène pour assurer la production de soufre élémentaire au lieu de sulfate. Ces réacteurs gagnent une certaine popularité dans la purification de divers flux gazeux contenant du H_2S comme le biogaz, les gaz d'échappement des usines de traitement des eaux usées, des fermes etc. Le garnissage du biofiltre est peu coûteux et peut contenir les nutriments nécessaires pour le développement et soutien des populations microbiennes. Les besoins de recherche dans ce domaine inclus l'optimisation de la biofiltration anaérobie, le développement d'un système qui prend avantage des caractéristiques des bactéries phototrophiques et chimiotrophiques et d'un système qui pourrait réaliser l'élimination simultanée du sulfure d'hydrogène et du siloxane. **Mots-clés**: sulfure d'hydrogène, phototrophique, chimiotrophique, oxydation biologique, biofiltration, épuration biologique.

INTRODUCTION

Hydrogen sulfide is present in biogas produced during the anaerobic digestion of biodegradable substances. It is produced from the degradation of proteins and other sulfur containing compounds present in the organic feed stock to the digester. The concentration of hydrogen sulfide in the biogas depends on the feedstock and varies between 0.1 to 2% (Lastella et al. 2002; Boyd 2000). Generally, biogas produced from manure and protein rich industrial wastes contain higher amounts of hydrogen sulfide (Schieder et al. 2003). Considerable amounts of hydrogen sulfide are also emitted from industrial activities such as petroleum refining (Henshaw et al. 1999), pulp and paper manufacturing (Wani et al. 1999), food processing, livestock farming (Chung et al. 2001), and natural gas processing (Kim et al. 1992). It is also found in landfill biogas and is the principal odorous component in off-gases from wastewater collection and treatment facilities (Cox and Deshusses 2001). Biogas derived from these waste stabilization processes is not usually used as a renewable energy source, but rather flared off as excess gas when it is not used for space and process heating (Tchobanoglous et al. 2003). One of the biggest factors limiting the use of biogas is related to the hydrogen sulfide it contains, which is very corrosive to internal combustion engines (Tchobanoglous et al. 2003; Ross et al. 1996). Currently, most commercial technologies for the removal of H_2S are chemically based and expensive to operate (Monteith et al. 2005; Gabriel and Deshusses 2003; Cha et al. 1999) thereby negating all of the financial incentives associated with potential revenues from energy produced in a cogeneration plant.

In addition to its unpleasant odor, hydrogen sulfide (H_2S) gas is highly toxic (Roth 1993). Upon inhalation, hydrogen sulfide reacts with enzymes in the bloodstream and inhibits

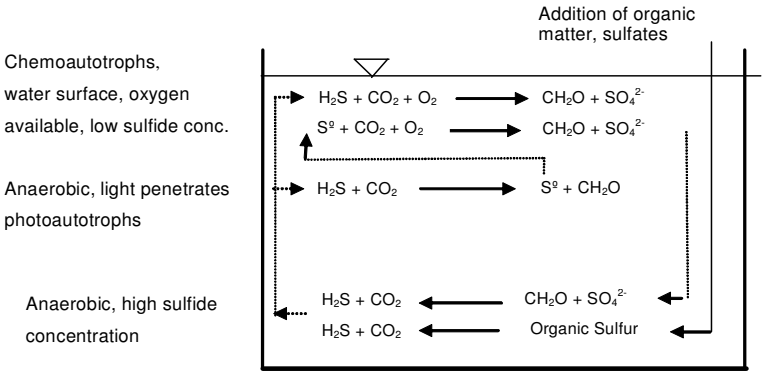

Fig. 1. Cycling of sulfur in a sulfuretum (adapted from Anderson 1978).

cellular respiration resulting in pulmonary paralysis, sudden collapse, and death. Continuous exposure to low (15-50 ppm) concentrations will generally cause irritation to mucous membranes and may also cause headaches, dizziness, and nausea. Higher concentrations (200-300 ppm) may result in respiratory arrest leading to coma and unconsciousness. Exposures for more than 30 minutes at concentrations greater than 700 ppm have been fatal (MSDS 1996).

Scrubbing, carbon adsorption, and chemical and thermal oxidation are used for H_2S removal from gas fluxes (Shareefdeen et al. 2002; Cha et al. 1999). The Claus process is one of the most popular processes used for hydrogen sulfide removal with sulfur recovery on an industrial scale (Kim and Chang 1991; Cooper and Alley 1986). In the first step of the Claus process, H_2S is partially oxidized to SO_2 with air. The H_2S/SO_2 mixture is then reacted over a bauxite catalyst to yield elemental sulfur (S^0) and water. Normally 90-95% of the H_2S is converted to S^0. The remaining H_2S is either oxidized to SO_2 or converted to sulfur in an off-gas treatment unit (Sittig 1978).

The chemical H_2S removal processes are expensive due to high chemical requirements, energy and disposal costs (Buisman et al. 1989). For these reasons, biological treatment methods for hydrogen sulfide removal are desirable as an alternative to chemical treatment (Sercu et al. 2005; Oyarzún et al. 2003). A biological hydrogen sulfide removal process has the potential to overcome some or all of the disadvantages of chemical processes (Elias et al. 2002; Kim et al. 2002).

This paper reviews current biological hydrogen sulfide removal processes in practice and identifies research needs for potential process improvement.

LITERATURE REVIEW

Bacteria used in bioreactors

Figure 1 shows conversions of different species of sulfur by naturally occurring bacteria where a complete oxidation to elemental sulfur is occurring. Such a situation often occurs in nature and is called a sulfuretum. A typical example is a pond in autumn where fallen leaves are the source of organic matter (Postgate 1968). Different bacteria tend to live in areas of the pond where their particular capabilities provide them with an ecological niche. Near the water surface, chemotrophic bacteria dominate where they can obtain their energy from the aerobic oxidation of H_2S and S^0 to form SO_4^{2-}. In the deep anaerobic zone, anaerobic decomposition of organic matter occurs and H_2S is produced. In the upper anaerobic zone where light can still penetrate and H_2S is available, growth of phototrophic bacteria occurs. These bacteria find suitable conditions for growth only in a narrow zone of overlap since sulfide and light occur in opposite gradients. In these narrow layers, they obtain reducing electrons from either H_2S or S^0 (Overmann 2001).

The desirable bacteria to be used in a bioprocess to convert H_2S to S^0 should possess the following basic features: reliable capability of converting H_2S to S^0, minimum nutrient inputs, and easy separation of S^0 from the biomass. Relevant photoautotrophs and chemotrophs are discussed below.

Photoautotrophs Studies on microbial ecology associated with phototrophic bacteria have shown that a species of green sulfur bacteria (GSB) *Cholorobium limicola* (originally called *Cholorobium limicola* forma *thiosulfatophilum* (Larsen 1952)) is the most suitable for sulfide removal and satisfies the criteria for a desirable bacterium (Syed and Henshaw 2003). *Cholorobium limicola* is capable of oxidizing sulfide to elemental sulfur, requires only light, CO_2, and inorganic nutrients for growth and is strictly anaerobic. GSB are non-motile and deposit elemental sulfur extracellularly. This feature makes GSB suitable where the recovery of elemental sulfur from sulfide-containing wastewater is desired. The overall photochemical reaction by which GSB oxidizes S^{2-} to S^0 while reducing CO_2 to carbohydrates is (van Niel 1931):

$$2nH_2S + nCO_2 \xrightarrow{\text{light energy}} 2nS^0 + n(CH_2O) + nH_2O \qquad (1)$$

Studies involving phototrophic bacteria are summarized in Table 1. Cork et al. (1985) introduced the concept of the "van Niel curve" by plotting the reactor feed rate as a function of irradiance (W/m^2) for their batch-fed reactor system (Fig. 2). The curve describes the relationship between S^{2-} loading rate and light intensity (radiant flux). When light intensity and sulfide flow rate were adjusted to a point on the curve (balanced loading), all of the sulfide introduced to the reactor was oxidized to elemental sulfur without the formation of sulfate. Under sulfide overloading conditions (to the right of the curve), light energy was not sufficient and sulfide accumulated in the reactor. When the reactor was in a sulfide underloading condition (to the left of the curve), the surplus light caused the formation of sulfate as shown by Eq. 2 (Larsen 1952).

$$nH_2S + 2nCO_2 + 2nH_2O \xrightarrow{\text{light energy}} nSO_4^{2-} + 2nH^+ + 2n(CH_2O) \qquad (2)$$

Therefore, only when the bioreactor system is adjusted to operate "on the curve", sulfide removal is complete and a maximum amount of elemental sulfur is produced.

The *in vivo* light absorption spectrum of *C. limicola* exhibits light absorption between 350 and 850 nm (Stanier et al. 1986) with a peak at 760 nm. The authors describe two different conditions under which the quality of light available is different. In shallow ponds, relatively rich in organic matter, except near

Table 1. Research conducted in hydrogen sulfide removal using photoautotrophs (adapted from Syed 2003).

Reference	Configuration*	Volume# (L)	Influent [H_2S]	S^{2-} loading (mg h^{-1} L^{-1})	Removal efficiency† (%)	Irradiance‡ (W/m^2)
Kobayashi et al. (1983)	FF, U	8	16 mg/L in liquid	0.59-1.27	81-92	NQ
Kobayashi et al. (1983)	FF, plug	0.1	19-24 mg/L in liquid	102-125	100	NQ
Cork et al. (1985)	SG, CSTR	0.8	Gas, concentration unknown	74-109	100	150-2000
Maka and Cork (1990)	SG, CSTR	0.8	1-2 mM in gas	32-64	90-100	139
Kim et al. (1991)	SG, CSTR	4	2.1 mM in gas	61	>99	1200
Kim et al. (1992)	SG, CSTR	4	2.1 mM in gas	64	100	1750
Kim et al. (1996)	SG, CSTR	11.9	1.45-1.87 mM in gas	14.6-19	99.8	15.2
Basu et al. (1996)	SG, CSTR	1.25	25,000 ppm in gas	94.4	>96.6	ID
Henshaw et al (1997)	SG, CSTR	13.7	90-550 mg/L in liquid	2.1-5.6	>90	258
Henshaw and Zhu (2001)	FF	0.02	141-380 mg/L in liquid	111-286	82-100	25.4
Syed and Henshaw (2003)	FF	0.0048	91-164 mg/L in liquid	1323-1451	100	152

* CSTR = continuously stirred tank reactor; FF = fixed-film; SG = suspended-growth; U = upflow

Volume = wet volume of reactor

† Removal efficiency = $(S^{=}_{in} - S^{=}_{out})/S^{=}_{in}$

‡ ID = insufficient data to calculate; NQ = not quantified

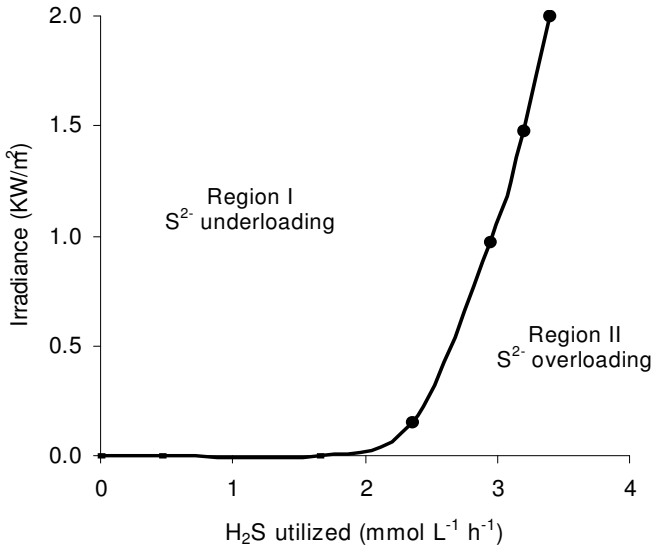

Fig. 2. van Niel Curve (adapted from Cork et al. 1985).

the air-water interface, the water is oxygen-free allowing green sulfur bacteria to grow close to the water surface. There they obtain light of long wavelength, which is transmitted through the overlying aerobic phototrophs, and the light, in the far red and near-infrared regions, used by the GSB for photosynthesis is almost entirely absorbed by bacteriochlorophylls. The second environment occurs in lakes where a warmer, aerobic layer covers a stagnant layer that is cold and oxygen-free. GSB grow in a narrow horizontal band, situated just within the anaerobic layer. In this case, the overlying water column acts as a light filter, transmitting only green and blue-green light, of wavelengths between 450 and 550 nm. Carotenoids become the dominant light harvesting pigments and the GSB in this environment typically contain a very high carotenoid content.

Chemotrophs A number of chemotrophs are suitable for the biodegradation of H_2S. These bacteria grow and produce new cell material by using inorganic carbon (CO_2) as a carbon source and chemical energy from the oxidation of reduced inorganic compounds such as H_2S. In the presence of reduced organic carbon sources (glucose, amino acids, etc.), some of these bacteria (so-called mixotrophic microorganisms) can grow heterotrophically, using the organic carbon as a carbon source and an inorganic compound as an energy source (Prescott et al. 2003).

Biodegradation of H_2S by chemotrophs occurs in aerobic conditions with O_2 as an electron acceptor or in anaerobic conditions with alternative electron acceptors (e.g. nitrate), depending on the type of bacteria (Prescott et al. 2003). Examples of energy sources for representative chemotrophs are presented in Table 2.

The metabolism of species such as *Thiobacillus, Thermothrix, Thiothrix, Beggiato* has been intensively studied for oxidation of inorganic (elemental sulfur, hydrogen sulfide, thiosulfate) or organic (methanethiol, dimethylsulfide, dimethyldisulfide) sulfur compounds (Stanier et al. 1986). These microorganisms grow in soil, aquatic habitats, activated sludge systems, etc. under aerobic, microaerophilic, and anaerobic conditions (Prescott et al. 2003; Postgate 1968). Characteristics of some of these microorganisms are presented in Table 3.

Table 2. Examples of energy sources for representative chemotrophs (Prescott et al. 2003).

Bacteria	Electron donor	Electron acceptor	Carbon source	Products
Thiobacilllus sp. (general)	S^0, H_2S, $S_2O_3^{2-}$	O_2	CO_2	SO_4^{2-}
Thiobacilllus denitrifcans	S^0, H_2S, $S_2O_3^{2-}$	O_2, NO_3^-	CO_2	SO_4^{2-}, N_2
Thiobacilllus ferrooxidans	Fe^{2+}, S^0, H_2S	O_2	CO_2	Fe^{3+}, SO_4^{2-}

Table 3. Characteristics of some microorganims implicated in degradation of H_2S or other sulfur compounds.

Conditions	Microorganisms								
	Thiobacillus ferrooxidans	*Thiobacillus thiooxidans*	*Thiobacillus novellus*	*Thiobacillus thioparus*	*Thiobacillus denitrificans*	*Thermothrix azorensis*	*Thiothrix nivea*	*Thioalkalispira microaerophila*	*Thiomicrospra frisia*
pH growth range	-	0.5 - 6.0	[a]5.7 - 9.0	5 - 9	-	6.0 - 8.5	6 - 8.5	8 - 10.4	4.2 - 8.5
Optimum pH	1.3 - 4.5	2.0 - 3.5	7.0	7.5	6.8 - 7.4	7.0 - 7.5	-	10	6.5
Temperature growth range (°C)	10 - 37	10 - 37	[a]10 - 37	-	-	63 - 86 (thermophile)	-	-	3.5 - 39
Optimum temperature (°C)	30 - 35	28 - 30	30	28	28 - 32	76 - 78	15 - 30	-	32 - 35
* G+C content of DNA (mol%)	56 - 59	-	67.2	62	63	39.7	44 - 55	58.9	39.6
Cells type	Gram-negative	Gram-negative	[a]Gram-negative	Gram-negative	-	Gram-negative	Gram-negative or Gram-variable	Gram-negative	Gram-negative
Group	-	-	[a]α-2 Proteobacteria	β-Proteobacteria	β-Proteobacteria	β-Proteobacteria	[b]γ-Proteobacteria	γ-Proteobacteria	γ-Proteobacteria
Spore formation	None	None	None	-	-	None	-	-	-
Motility	0 to several polar or petrichous flagella	-	Non-motile	Motile	Motile by means of a polar flagellum	Motile	No flagella	Motile by means of a single polar flagellum	Motile
Shape	Rod, 0.5-1.0 µm	Rod, 0.5 x 1.1-2.0 µm	Rod, 0.4-0.8 x 0.8-2.0 µm	Rod, 0.9-1.8 µm	Rod, 0.5 x 1.0-3.0 µm	Rod, 0.3-0.8 x 2-5 µm	Rod, 0.7-2.6 x 0.7-5.0 µm	Spirillum, 0.3-0.45 x 1-4 µm	Bent-rod, 0.3-0.5 x 1.0-2.7 µm
Trophy	Obligate chemoautotroph	Obligate chemoautotroph	Mixotroph (faculative chemoautotroph)	Obligate chemoautotroph	Obligate chemoautotroph	Obligate chemoautotroph	Mixotroph (faculative chemoautroph)	Obligate chemoautotroph	Obligate chemoautotroph
Examples of energy source	Ferrous ion and reduced sulfur compounds	Hydrogen sulfide, polithionates, elemental sulfur	Hydrogen sulfide, methyl mercaptan, dimethyl sulfide, dimethyl disulfide	Thiosulfate, sulfide	Thiosulfate, tetrathionate, thiocyanate, sulfide, elemental sulfur	Thiosulfate, tetrathionate, hydrogen sulfide, elemental sulfur	Inorganic sulfur compounds, simple organic compounds, sugars	Sulfide, polysulfide, elemental sulfur, thiosulfate	Thiosulfate, tetrathionate, sulfur, sulfide
Oxygen requirement	Facultative anaerobe**	Strictly aerobe	[a]Strictly aerobe	Strictly aerobe	Faculataive anaerobe***	Strictly aerobe	Strictly aerobe and microaerophile	Strictly aerobe and microaerophile	Strictly aerobe
Sulfur deposit	-	-	-	Extracellular	-	Intracellular	Intracellular	Intracellular	Extracellular
Reference	Colorado School of Mines[¶]	Takano et al. (1997)	Cha et al. (1999) [a]Kelly et al. (2000)	Vlasceanu et al. (1997)	Kelly and Wood (2000)	Odintsova et al. (1996)	Howarth et al. (1999), [b]Prescott et al. (2003)	Sorokin et al. (2002)	Brinkhoff et al. (1999)

* G = guanine; C = cytosine

** Under anaerobic conditions, *T. ferroosidans* can grow on elemental sulfur using ferric iron as an electron acceptor.

*** Grows as an anaerobic chemoautroph by using nitrate, nitrite, or nitrous oxide.

[¶] http://www.mines.edu/fs_home/jhoran/ch126/thiobaci.htm (2006/02/16)

Table 4. Reactions involving chemotrophic bacteria.

Bacteria	Reaction mechanism	Reference
Thiobacillus thioparus	$2HS^- + O_2 \rightarrow 2S^0 + 2OH^-$ $2S^0 + 3O_2 + 2OH^- \rightarrow 2SO_4^{2-} + 2H^+$	Chung et al. (1996)
	$H_2S + 2O_2 \rightarrow SO_4^{2-} + 2H^+$	Kim et al. (2002)
Thiobacillus denitrificans	$3HS^- + 3.9NO_3^- + 0.2NH_4^+ + HCO_3^- + 1.7H^+ \rightarrow CH_{1.8}O_{0.5}N_{0.2} + 1.9N_2 + 3SO_4^{2-} + 2.3H_2O$ $14.5HS^- + 5NO_3^- + 0.2NH_4^+ + HCO_3^- + 20.3H^+ \rightarrow CH_{1.8}O_{0.5}N_{0.2} + 2.5N_2 + 14.5S + 27.4H_2O$	Kleerebezem and Mendez (2002)
	$55S + 20CO_2 + 50NO_3^- + 38H_2O + 4NH_4^+ \rightarrow 4C_5H_7O_2N + 25N_2 + 55SO_4^{2-} + 64H^+$	Lampe and Zhang (1996)
	$5HS^- + 8NO_3^- + 3H^+ \rightarrow 5SO_4^{2-} + 4N_2 + 4H_2O$	McComas and Sublette (2001)
Thiobacillus ferrooxidans	$2FeSO_4 + H_2SO_4 + 1/2\ O_2 \rightarrow Fe_2(SO_4)_3 + H_2O$	Mesa et al. (2002)
	$2FeS_2 + 7.5O_2 + H_2O \rightarrow Fe_2(SO_4)_3 + H_2SO_4$	Takano et al. (1997)

Thiobacillus sp. is widely used in studies of the conversion of H_2S and other sulfur compounds by biological processes (Oyarzún et al. 2003; Cha et al. 1999; Chung et al. 1996; Sublette and Sylvester 1987). These bacteria have the ability to grow under various environmental stress conditions such as oxygen deficiency, acid conditions, etc. Many *Thiobacillus sp.* (i.e. *T. thiooxidans*, *T. ferrooxidans*) have acidophilic characteristics and are able to develop in conditions of low pH (1-6). *Thiobacillus thiooxidans* has a great tolerance for acidic conditions and can grow at pH < 1 (Devinny et al. 1999; Takano et al. 1997). Thiobacilli such as *T. thiooxidans* and *T. ferrooxidans* are used in processing digested sludge or leaching low-grade metal ores because of their ability to remove metals by microbial leaching (Sreekrishnan and Tyagi 1996; Prescott et al. 2003). Other *Thiobacillus* sp. (e.g. *T. thioparus, T. denitrificans, T. novellus*) develop in neutral medium (neutrophilic bacteria) at pH of 6-8. *Thiobacillus denitrificans* is able to grow facultatively on reduced sulfur compounds by reducing nitrate (NO_3^-) to nitrogen gas (N_2) (Kleerebezem and Mendez 2002; Lampe and Zhang 1996). *Thiobacillus novellus* is a mixotroph Thiobacilli because it can grow heterotrophically (Kelly at al. 2000).

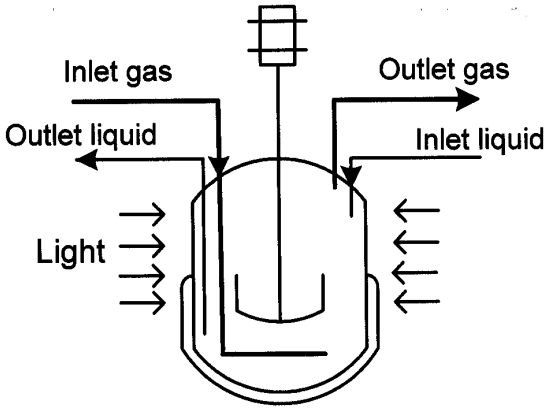

Fig. 3. Fed-batch or continuous flow reactor.

Other species are able to degrade sulfur compounds in neutrophilic, alkaline, or thermophilic conditions. *Thermothrix azorensis* and *Thiothrix nivea* are neutrophilic bacteria and develop well at pH of 6-8 (Odintsova et al. 1996; Howarth et al. 1999). Optimum growth temperature for *Thermothrix azorensis*, a thermophilic bacterium, is between 76 and 86ºC (Odintsova et al. 1996). *Thioalkalispira microaerophila* is able to grow in alkaline conditions and attains optimum growth at pH 10 (Sorokin et al. 2002).

Beggiatoa sp. and *Thiothrix* sp., both microaerophilic γ-Proteobacteria, have mixotrophic nutritional function because they are able to degrade H_2S using inorganic and organic (e.g. acetate) energy sources (Prescott et al. 2003; Howarth et al. 1999). *Pseudomonas acidovorans* and *Pseudomonas putida* are other mixotrophs which degrade both H_2S and organosulfur compounds (Oyarzún et al. 2003; Chung et al. 2001).

The reaction shown in Eq. 3 takes place in an aerobic sulfide removal system (Kuenen 1975).

$$H_2S + CO_2 + nutrients + O_2 \xrightarrow{chemotrophs} cells + S\ and\ /\ or\ SO_4^{2-} + H_2O \quad (3)$$

Under oxygen limiting conditions, sulfur is the major end product, while sulfate is formed when sulfide is limited. Other relevant reactions are shown in Table 4**.**

Bioreactors for H_2S removal involving phototrophic bacteria

Gas-fed batch reactor Typically a gas fed batch reactor (Fig. 3) is a stirred tank type reactor, continuously or intermittently operated for the gas phase (the target flux) and cyclically operated for the liquid phase (nutritive solution). The microorganisms can be suspended in the solution or immobilized on different media (i.e. strontium alginate beads, Kim and Chang 1991).

Maka and Cork (1990) investigated the effects of light quantity and intensity on H_2S metabolism in a gas fed-batch

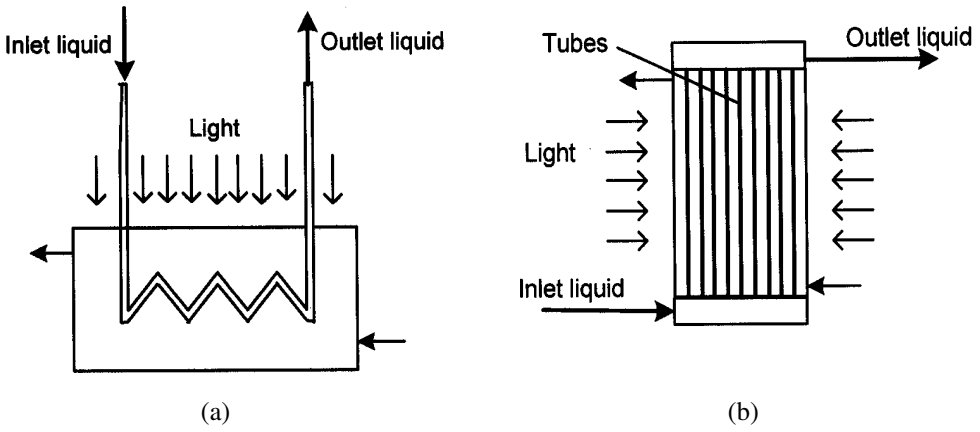

Fig. 4. Phototube reactors: (a) horizontal; (b) vertical.

reactor utilizing GSB. In this experiment, the intensity of the light source was varied, keeping the exposed area of the reactor constant at loading rates of 32 or 64 mg S^{2-} h^{-1} L^{-1}. A high irradiance resulted in sulfide removal, over half of which was converted to sulfate. At low irradiance, sulfide was not fully oxidized and accumulated in the reactor. Between these limits, a state in which neither sulfide nor sulfate was found in the reactor, elemental sulfur and thiosulfate ($S_2O_3^{2-}$) were the only products. For white light (380 to 900 nm) this optimum state resulted in 60% of the influent H_2S becoming S^0 and 40% becoming $S_2O_3^{2-}$. For infrared light (700 to 900 nm), the optimum favored sulfur production was 97:3 (S^0: $S_2O_3^{2-}$). The optimum for infrared light also occurred at a lower irradiance level (219 W/m^2) than white light (406 W/m^2). These findings demonstrated the superiority of infrared light as a light source to produce elemental sulfur using green sulfur bacteria.

Kim and Chang (1991) studied the bioconversion of hydrogen sulfide to elemental sulfur by *C. limicola* in an immobilized-cell reactor and a sulfur settling tank with a free cell recycle reactor. In the first reactor, cells were immobilized in strontium alginate beds and in the second reactor, the produced sulfur was removed by gravity settling and the medium was recycled to the fed-batch reactor. In comparison with the free cells, the immobilized cells required 30% less light energy at a H_2S removal rate of 68 mg h^{-1} L^{-1} initially but after 40 hours, the deterioration of the H_2S removal efficiency became significant due to the accumulation of sulfur in the beds. Subsequently, Kim et al. (1992) compared sulfide removal rates in 2-L and 4-L reactors. The difference in sulfide removal rates between 2-L and 4-L reactors (0.11 and 0.07 mg H_2S/h per milligram of protein, respectively) was explained by the higher light attenuation in the larger reactor since light intensity decreased exponentially with the penetration depth. They also observed that the average diameter of sulfur aggregates was 10 times that of bacterial cells.

Basu et al. (1996) used a continuous stirred tank reactor equipped with a sulfur separator to remove hydrogen sulfide from a gas stream containing 2.5% H_2S at 1 atmosphere pressure. At a sulfide loading rate of 94.4 mg h^{-1} L^{-1}, H_2S conversion by *Chlorobium thiosulfatophilum* ranged from 53% at a gas retention time of 12.2 min to 100% at a gas retention time of 23.7 min. The sulfur recovered from the process by gravity separation was 99.2% of the theoretical yield. The separation of elemental sulfur from the bioreactor contents is essential to realize its value as a chemical industry feedstock.

Kim et al. (1991) tried to optimize light energy input by using light emitting diodes (LEDs) with a peak wavelength at 710 nm in a batch-fed stirred tank reactor. Experiments were performed separately using an incandescent bulb, LED_{710}, and a combination of LED_{710} and a fluorescent bulb as the light sources and their individual performances (H_2S removal per unit luminous flux, (mmol/min) per (g protein/L) per (W/m^2)) were evaluated. They found that the maximum performances using LED_{710} and LED_{710} with fluorescent bulb were 18.7 and 14.1 times, respectively, the performance of a reactor with an incandescent bulb.

Later, Kim et al. (1996) investigated the performance of LEDs in a plate type photo-bioreactor. They observed that the maximum performance per unit luminous flux while using LEDs was 31 times that of an incandescent bulb. This efficiency was achieved by only supplying light within the wavelength range where absorption by bacteria was at a maximum.

Continuous-flow reactor In a continuous flow reactor (Fig. 3) the influent (gas or liquid) is continuously fed into the reactor at the same rate it is removed from the reactor. The reactor's contents are stirred continuously.

Using the effluent of a continuous-flow stirred-tank bioreactor, Henshaw et al. (1997) tested separation of the sulfur by settling, settling at elevated pH, filtration, and centrifugation. Centrifugation produced the best separation results; 90% of the elemental sulfur and 29% of the bacteria were removed from the suspension. They noted that a continuous-flow suspended-growth bioreactor system for sulfide removal/sulfur recovery required two separation stages, one to separate S^0 from the bioreactor effluent and one to separate biomass from the liquid product of the first separator. A fixed-film reactor can eliminate or lessen the need for two separators since the biomass remains in the reactor.

Phototube reactors Two types of phototube reactors are shown in Figs. 4a and 4b. These are tubular type reactors that are continuously operated. The reactor can be horizontally oriented (Fig. 4a) having several passes or spirals to improve the residence time in the reactor (Kobayashi et al. 1983) or can be vertically oriented, as presented in Fig. 4b (Syed and Henshaw 2003; Henshaw et al. 1999). The material of the tube is transparent to light and impermeable to oxygen (Syed and Henshaw 2003). Bacteria develop on the inner wall of the tube reactor (fixed-film reactor).

Kobayashi et al. (1983) used a "phototube" reactor in which a sulfide containing reactor was passed through a 12.8 m long, 3.2 mm ID Tygon tube which was immersed in an illuminated water bath. The tube was able to achieve 95% sulfide removal in about 24.6 min while operated at a sulfide loading rate of 67 mg h^{-1} L^{-1}.

Postulating that a vertical attached growth configuration could eliminate or significantly reduce the problem of sulfur accumulation encountered by Kim and Chang (1991), Henshaw et al. (1999) tested the ability of GSB to grow on six different transparent plastic tube materials to determine which medium would be best as a support medium in a vertical flow fixed-film bioreactor. Tygon was found superior to the other materials tested in terms of number of bacteriochlorophyll per unit surface area and low oxygen permeability. Bacteriochlorophyll was used as a measure of GSB biomass.

Using a fixed film, continuous-flow photobioreactor employing *C. limicola* and a infrared light source, Henshaw and Zhu (2001) succeeded in removing sulfide from synthetic wastewater at a sulfide loading rates of 111 to 286 mg h^{-1} L^{-1}, while 92 to 95% of the influent sulfide was converted to elemental sulfur. A fixed-film reactor was selected because of its ability to retain biomass for further sulfide oxidation. In this process, light can easily be transmitted to the biomass adhering to the inside of the transparent tubes whereas in a suspended growth process, light can be considerably attenuated at the center of the reactor. In subsequent experiments, Syed and Henshaw (2003, 2005) investigated the effects of tube size and light quality on H_2S removal. They observed that the smallest diameter tube reactor achieved the highest sulfide removal at the same light intensity (of infrared bulb and LEDs). A higher sulfide loading rate was achieved when LEDs providing light matching the peak absorption spectrum of GSB were the light source. The reactor system can be used for removal of gaseous H_2S after dissolving it in water.

Bioreactors for H_2S removal involving chemotrophic bacteria

A number of studies, summarized in Table 5, have been conducted using chemotrophic bacteria.

Gas-fed batch reactors Janssen et al. (1995) used two batch-fed reactors to study the oxidation of sulfide using a mixed culture of *Thiobacilli*. Pure oxygen was supplied to the reactors. The maximum sulfur production (73 ± 10%) occurred at an oxygen to sulfide ratio of 0.6 to 1.0 mol L^{-1} h^{-1}/ mol L^{-1} h^{-1}. At lower oxygen to sulfide ratios, the lower biological oxidation capacity resulted in the production of more thiosulfate. At higher oxygen to sulfide ratios, more sulfate was produced because more energy was consumed for bacterial growth than for the formation of elemental sulfur.

Continuous-flow reactors Sublette and Sylvester (1987) reported on a continuous stirred-tank reactor (CSTR) system using *Thiobacillus denitrificans* to remove H_2S from gas streams. Ninety-seven percent of the H_2S bubbled was removed and oxidized to sulfate.

Buisman et al. (1990) tested three different continuous-flow reactor configurations: fixed-film CSTR, biorotor (a rotating cage containing reticulated polyurethane biomass support particles, partly immersed in the reactor liquid), and a fixed-film upflow reactor. For the upflow and biorotor reactors, 95 to 100% sulfide removal efficiencies were achieved for loading rates up to 500 mg H_2S h^{-1} L^{-1}. The removal efficiency decreased rapidly above this loading rate. At 938 mg h^{-1} L^{-1} (biorotor) and 1040 mg h^{-1} L^{-1} (upflow) loadings, sulfide removal efficiencies were 69 and 73%, respectively. At a 500 mg h^{-1} L^{-1} sulfide loading rate, the stirred-tank reactor's removal efficiency was approximately 62%.

Bioscrubbers Removal of H_2S using bioscrubbers (Fig. 5a) involves a two stage process, firstly absorption of H_2S by a liquid followed by biological oxidation of H_2S in the liquid.

Nishimura and Yoda (1997) used a multiple bubble-tray air-tight contact tower (bioscrubber) to scrub hydrogen sulfide from the biogas produced by an anaerobic wastewater treatment process. A two-reactor system (a gas-liquid contact tower and an aeration tank) were used to separate the oxidation process from the absorption process to prevent air from mixing with the biogas. Mixed liquor from the activated sludge process was continuously fed to and withdrawn from the contact tower. In the contact tower, H_2S from the biogas was absorbed into the mixed liquor and subsequently oxidized to sulfate by sulfur oxidizing bacteria after returning to the aeration tank. Based on their preliminary results, a full scale plant treating potato processing wastewater was constructed. When treating 2000 ppm of H_2S in 40 m^3/h of biogas, more than 99% removal efficiency was achieved.

Mesa et al. (2002) described a bioscrubber system which can be integrated into a system to remove H_2S from biogas by a combination of chemical and biological processes. H_2S removal can be achieved by absorption in a ferric sulfate solution producing ferrous sulfate and elemental sulfur. Ferric sulfate can be regenerated by biological oxidation using *Acidithiobacillus ferrooxidans*. Relevant reactions are shown in Table 4. The study investigated the oxidation of ferrous iron by *A. ferrooxidans* which was immobilized on a polyurethane foam support and the support particles placed in an aerated column. Ferric precipitates were accumulated on the support and on the air diffusers which necessitated periodic interruptions of the process for cleaning. Precipitation, air supply, and chemical cost are the potential constraints for this process.

A full scale plant located northeast of Brooks, Alberta, Canada uses Shell-Paques® process for natural gas desulfurization (Benschop et al. 2002). H_2S is removed from a gaseous stream by absorption into a sodium carbonate/bicarbonate solution. The sulfide containing scrubbing liquid is treated in the bioreactor where it is mostly converted biologically to elemental sulfur. The bioreactor is supplied with a nutrient stream, air, make-up water, and sodium hydroxide. It is reported that normally less than 3.5% of the sulfide is converted to sulfate and a continuous bleed stream is required to avoid accumulation of sulfate. A compost filter is used to treat the trace H_2S present in the spent air from the bioreactor. Less than 4 ppmv effluent H_2S concentration is achieved when treating natural gas containing 2000 ppmv H_2S.

Biofilter A biofilter (Fig. 5b) is a three phase bioreactor (gas, liquid, solid) made with a filter bed that has a high porosity, high buffer capacity, high nutrient availability, and high moisture retention capacity to ensure that the target microorganisms can grow on it (Elias et al. 2002; Jorio and Heitz 1999; Daustos et al. 2005). The contaminated gas is continuously fed in the biofilter, while a nutrient solution is discontinuously added. Various types of biofilter media have been used by researchers. Representative cases are discussed below.

Table 5. Research conducted on hydrogen sulfide removal using bioscrubbers/biofilters or biotrickling filters.

Scale	Process type	Type bed	Bed volume	Pollutants treated and inlet gas concentration	Gas flow rate and empty bed residence time (EBRT)	Bacteria	Removal efficiency	Innoculation	Reference
Laboratory	Biofiltration	Cell-laden Ca-alginate	0.7 L	5-100 ppm H_2S, balance air	18-150 L/h	*T. thioparus*	85-99% (H_2S)	Immobilization of *T. thioparus* on Ca-alginate	Chung et al. (1996)
Full	Bioscrubbing: anerobic absorption + aerobic biooxidation	Activated sludge	3 m^3 (scrubber) 550 m^3 (aeration tank)	Biogas from waste-water treatment plant: 300-2000 ppm H_2S, 80% CH_4, 20% CO_2	40 m^3/h	Indigenous (*Thiobacillus sp.*, etc.)	>99% (H_2S)	-	Nishimura and Yoda (1997)
Laboratory	Biooxidataion in the bubble column reactor	Poly-4-vinylpyridine (PVP) matrix	6.3 L (reactor volume)	Mixed gas composed of 30 ppm H_2S, MM, DMS, and DMDS*	-	*T. novellus*	100% (H_2S) 100% (MM) 87% (DMDS) 73% (DMS)	Immobilization of *T. novellas* on PVP matrix)	Cha et al. (1999)
Laboratory	Biofiltration	Compost or compost/hog fuel	18 L	10-450 ppm H_2S, balance air	1.7 m^3/h 38s	Indigenous (in sludge)	90-100% (H_2S)	Yes (waste-activated sludge)	Wani et al (1999)
				10-450 ppm H_2S, 10.8 ppm DMS, 6.6 ppm DMDS, balance air			90-100% (H_2S) 30-35% (DMS) <30% (DMDS)		
Laboratory	Biofiltration	Cell-laden Ca-alginate	0.7 L	60-120 ppm H_2S, 60-120 ppm NH_3, balance air	36 L/h 72 s	*Pseudomonas putida* (for H_2S) *Arthrobacter oxydans* (for NH_3)	>90% (H_2S) >95% (NH_3)	Co-immobilization of *P. putida* and *A. oxydans* on Ca-aglinate	Chung et al. (2001)
Laboratory	Biotrickling	Polypropylene pall rings	10 L	170 ppm H_2S, 2.2 g/m^3 toluene, balance air	1 m^3/h 36 s	Toluene-degraders sulfide oxidizing bacteria	100% (H_2S) 25-75% (toluene)	Yes (biomass from a toluene-degrading biotrickling filter)	Cox and Deshusses (2001)
Laboratory	Biofiltration	Pig manure + sawdust	5.9 L	10-45 g H_2S m^{-3} h^{-1}, balance air	13.5-27 s	Indigenous	>90% (H_2S)	No	Elias et al. (2002)
Pilot	Biotrickling	-	3.8 m^3	Emissions from wastewater treatment plants: 10-50 ppm H_2S, 0-150 ppb VOC, traces of other compounds	650 m^3/h 21 s	-	98% (H_2S) 50-70% (VOC)	-	Cox and Deshusses (2002)
Full	Biotrickling	Structured plastic packing	51 m^3	Exhaust air from a cellophane plant: 60-155 ppm H_2S, 35-100 mg/m^3 CS_2	44,200 m^3/h (total flow) 4-10 s	-	85-99% (H_2S) 40-70% (CS_2)	-	Cox and Deshusses (2002)

Table 5. continued

Full	Biotrickling/ Biofiltration	Polyurethane foam	500 m^3 (6 units)	Odors from tobacco company: 800-1200 OU	11 s	-	>90% (H_2S)	-	Cox and Deshusses (2002)
Laboratory	Biofiltration	Wood chips, granular activated carbon (GAC)	1 L	30-450 ppm H_2S, 35-200 ppm NH_3, balance air	60-180 L/h 20-60 s	*T. thioparus* Nitrifying bacteria	75-99% (H_2S) 30-92% (NH_3)	Yes (activated sludge from sewage water treatment plant + culture of *T. thioparus*)	Kim et al. (2002)
Laboratory	Biooxidation in the fixed film reactor	Polyurethane particles	1 L	Effluent from a gas lift reactor treating a sulfide nitrate mixture (2-20 mM as S-tot)	-	*T. tenitrificans* Nitrifying bacteria	>80% (S-tot)	-	Kleerebezem and Mendez (2002)
Full	Biosscrubbing (absorption +aerobic biooxidation) + separate biofiltration	Alkaline solution for scrubbing Compost for biofiltration	-	Natural gas: 2000 ppm H_2S	322,000 nm^3/d	Indigenous	>99.8% (H_2S)	-	Benschop et al. (2002)
Full	Biofiltration	Wood-based medium	Open bed biofilter	Odorous air from meat rendering plant (24,544 OU): 1.07 mg H_2S/m^3, 5.2 mg NH_3/m^3, 0.66 mg/m^3 methanethol, 1.2 mg/m^3 ethylamine, 775.25 mg/m^3 DMS	25485 m^3/h 30 s	Indigenous	>96% (all compounds, with exception of methanethiol, 70%)	No	Shareefdeen et al. (2002)
Full	Biotrickling	Polyurethane foam	7.3 m^3	Odorous air from wastewater treatment plant: 5-25 ppm H_2S, 67 ppb carbonyl sulfide, 192 ppb MM, 70 ppb CS_2 (4000 ppm CO_2)	1.6-2.3 s	*Thiobacillus sp.*	>97% (H_2S) 67% (MM) 44% (carbonyl sulfide) 35% (CS_2)	Yes (activated sludge from wastewater treatment plant)	Gabriel and Deshusses (2003)
Laboratory	Biofiltration	Granulated sludge	10 L (column)	170-680 g H_2S m^{-3} d^{-1}, 86-340 g NH_3 m^{-3} d^{-1}, balance air	-	Nitrifying bacteria, Sulfide oxidizing bacteria	100% (H_2) 80% (NH_3)	Yes (acclimatized sludge)	Malhautier et al. (2003)
Laboratory	Biofiltration	Mature compost	8 L	50 ppm H_2S, balance air	10 L/min	Indigenous	90-100% (H_2S)	No	Morgan-Sagastume et al. (2003)
Laboratory	Biofiltration	Peat	1 L	355-1400 ppm H_2S, balance air	30 L/h	*T. thioparus*	65-100% (H_2S)	Yes (culture of *T. thioparus*)	Oyarzún et al. (2003)
Full	Biofiltration	-	-	Biogas from anaerobic wastewater treatment plant (5000 ppm H_2S)	10-350 m^3/h	Thiobacteria *(Thiobacillus sp.)*	>90% (H_2S)	Yes (activated sludge from digester)	Schieder et al. (2003)

* MM = methyl mercaptan; DMS = dimethyl sulfide; DMDS = dimethyl disulfide

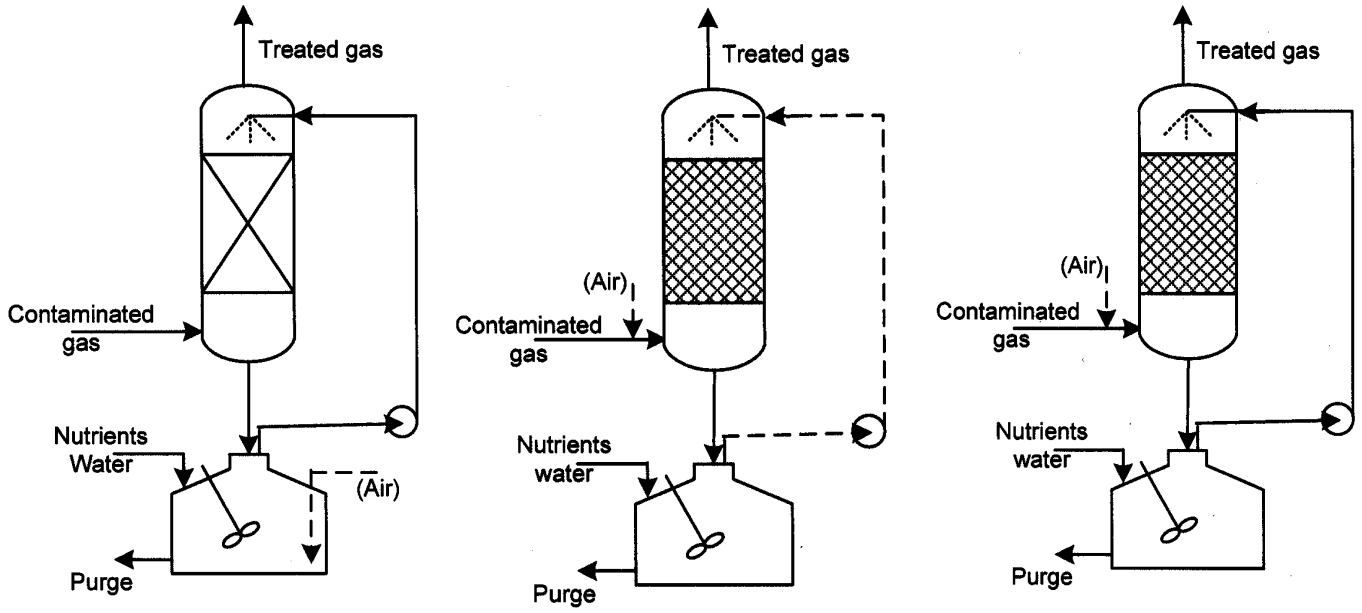

Fig. 5. Systems for removal of H_2S: (a) bioscrubber; (b) biofilter; (c) biotrickling filter.

Chung et al. (1996) immobilized *Thiobacillus thioparus* CH11 with Ca-alginate producing pellet packing material for the biofilter. At a 28 second optimal retention time, the H_2S removal efficiency was more than 98%. Elemental sulfur or sulfate was produced depending on the inlet H_2S concentration. Chung et al. (1997) used *Thiobacillus novellus* in a biofilter for H_2S oxidation under mixotrophic conditions. A removal efficiency of 99.6% was achieved and the products were sulfate (83.6%) and sulfite (12.6%). Little conversion of sulfide to elemental sulfur was achieved. Later, Chung et al. (2001) used biofilters packed with co-immobilized cells *Pseudomonas putida* CH11 and *Arthobacter oxydans* CH8 for removal of H_2S and NH_3, respectively, which are often present in off-gases of a livestock farm. In the 5-65 ppm range, H_2S and NH_3 removal efficiencies were greater than 96%. However, at higher concentrations, H_2S and NH_3 showed inhibitory effects on H_2S removal. They also assessed the environmental risk associated with the release of bacteria when treating large volumes of waste gases. The exhaust gas contained small amounts of bacteria (< 19 CFU/m^3 in all cases) and was considered safe.

Wani et al. (1999) described the removal characteristics of H_2S and other reduced sulfur compounds emitted from kraft pulp mills using three different biofilter mediums: compost, hog-fuel (pulverized mixture of raw bark, wood waste, and other materials) and a mixture of compost and hog fuel at 1:1 (w/w) ratio. Dolomitic lime was mixed with each medium to act as a pH buffer. No significant difference was observed in the H_2S elimination capacities of these three media. However, the pH of the media decreased significantly over an operating period of more than six months. At H_2S concentrations up to 250 ppmv, complete removal was observed. The removal efficiency for inlet concentrations higher than 250 ppmv was above 90%. Compost, hog-fuel, and the mixture media had maximum elimination capacities of 136, 137, and 138 g m^{-3} h^{-1}, respectively.

A comparison between removal efficiencies of inorganic (H_2S) and organo-sulfur (methyl mercaptan, dimethyl sulfide, and dimethyl disulfide) odour compounds by immobilized *T. novellus* is presented in the study of Cha et al. (1999). They observed *T. novellus* can degrade H_2S > methyl mercaptan > dimethyl disulfide > dimethyl sulfide and the removal efficiency was 100% for H_2S and methyl mercaptan, 87% for dimethyl disulfide, and 73% for the dimethyl sulfide. The final metabolic product was sulfate.

Shareefdeen et al. (2002) reported the operation of a commercial biofilter for the treatment of an air stream containing hydrogen sulfide, ammonia, dimethyl sulfide, methanethiol, and ethylamine. This proprietary wood-based (BIOMIX™) biofilter achieved 96.6% removal of H_2S at an inlet concentration of 1.07 mg/m^3.

Elias et al. (2002) used packing material made up of pig manure and sawdust for biofiltration purposes. More than 90% H_2S removal efficiency was attained at a loading rate of 45 g m^{-3} h^{-1}. No nutrient was added to the system and the porosity of the packing material decreased from 23.1 to 12.9%. However, this change in porosity did not affect the removal efficiency significantly and it was claimed that the biofilter could be easily cleaned by flushing water through the inlet. The main by-product of the biodegradation process was sulfur (82% of total sulfur accumulation), accompanied by sulfates and thiosulfates (<18%).

Kim et al. (2002) investigated the simultaneous removal of H_2S and NH_3 using two biofilters, one packed with wood chips and the other with granular activated carbon (GAC). A mixture of activated sludge (as a source of nitrifying bacteria) and *Thiobacillus thioparus* (for sulfur oxidation) was sprayed on the packing materials and the drain solution of the biofilter was recirculated to increase the inoculation of microorganisms. Initially both of the filters showed high (99.9%) removal efficiency. However, due to the accumulation of elemental sulfur and ammonium sulfate on the packing materials removal

efficiency decreased over time to 75 and 30% for H_2S and NH_3, respectively.

Kleerebezem and Mendez (2002) proposed the simultaneous degradation of H_2S and NH_3 using *T. denitrificans* and nitrifying bacteria. *Thiobacillus denitrificans* is able to degrade H_2S in both aerobic and anaerobic conditions using oxygen or nitrate as an electron acceptor. Nitrate (NO_3^-) can be obtained from the nitrification of ammonia by nitrifying bacteria. *Thiobacillus denitrificans* simultaneously oxidizes H_2S to elemental sulfur or sulfate and reduces nitrate to nitrogen gas. Stoichiometric equations for autotrophic denitrification by *T. denitrificants* are presented in Table 4 (Kleerebezem and Mendez 2002; Lampe and Zhang 1996).

Malhautier et al. (2003) also performed an experiment involving H_2S and NH_3 using two laboratory scale biofilters packed with granulated digested sludge. One unit was fed mainly with H_2S and the other unit with NH_3. Complete H_2S removal (100%) was obtained and no influence on NH_3 or H_2S removal was observed. An 80% NH_3 removal efficiency was obtained, however, the authors concluded that the oxidation of high levels of H_2S might have a negative effect on the growth and activity of nitrifying bacteria.

Morgan-Sagastume et al. (2003) investigated changes in the physical properties of a compost biofilter treating hydrogen sulfide. Bench-scale biofilter columns filled with compost media consisting of mature compost derived from food, leaf, yard waste, and horse manure were used. H_2S removal efficiency decreased from 100 to 90% over 206 days of operation. They concluded that the variation in moisture content and specific surface area can explain the decrease in removal efficiency over time. They also mentioned that SO_4^{2-} accumulation which reduced the pH of the compost media from 7.5 to 4.5 could be an important factor. After re-mixing of the compost media, the H_2S removal efficiency returned to near 100%.

Oyarzún et al. (2003) used peat for the filter bed of a biofiltration system inoculated with *Thiobacillus thioparus*. Supplemental nutrient was added and the initial moisture content was adjusted to 92%. The pH was also adjusted to 6.0. Full removal was achieved when fed with 355 ppm H_2S at 0.03 m^3/h. The removal efficiency decreased with increasing inlet H_2S concentrations and a maximum removal capacity of 55 g m^{-3} h^{-1} was obtained.

Schieder et al. (2003) described the "BIO-Sulfex" biofilter to remove H_2S from biogas which uses thiobacteria attached on fixed bed material. The biomass was aerated and the filter was flushed with nutrient containing liquid to remove sulfur from the system. Six BIO-Sulfex modules to treat biogas containing up to 5000 ppm H_2S were operated at flowrates of 10 to 350 m^3/h with 90% or more H_2S removal achieved.

Clark et al. (2004) operated a pilot-scale agricultural biofilter to reduce odours from a swine manure treatment plant's exhaust air. Biofilters were packed with polystyrene particles and peat moss (3:1 ratio by volume). The packing volume was 1.89 m^3. The gas flowrate was 100 L/s. The inlet load contained 2-60 ppm hydrogen sulfide and 2-30 ppm ammonia. The addition of nutrients did not play an important role in the overall system performance. Average odour reduction was approximately 38% without addition of nutrients and 45% when nutrients were added. Increasing the temperature had a favourable effect during the acclimatisation phase only.

Biotrickling filter. The working principle of a biotrickling filter (Fig. 5c) is the same as for a biofilter except that the packed bed is continuously trickled over by an aqueous phase nutritive solution (Cox and Deshusses 2001).

Cox and Deshusses (2001) used two laboratory scale biotrickling filters made of polypropylene, inoculated with biomass from a toluene biodegrading filter operating at pHs of 7.0 and 4.5 to treat H_2S and toluene in a gas stream. There was no significant difference between the performances of the two reactors in terms of H_2S removal. At an inlet concentration of approximately 50 ppmv, complete consumption of H_2S was observed. However, the removal efficiency decreased to 70-80% when the inlet concentrations were raised to 170 ppmv.

High removal efficiency for H_2S, in comparison to other reduced sulfur compounds was obtained by Gabriel and Deshusses (2003) (Table 5) using *Thiobacillus sp*. in a biotrickling filter. For inlet H_2S concentrations as high as 30 ppmv, typical removal efficiency was 98%. Methyl mercaptan, carbonyl sulfide, and carbon disulfide removal efficiencies were 67, 44, and 35% at inlet concentrations of 67, 193, and 70 ppbv, respectively.

Sercu et al. (2005) studied the aerobic removal of hydrogen sulfide using a biotrickling filter packed with 1L-polyethylene rings (73% volume free) inoculated with *Acidithiobacillus thiooxidans* ATCC-19377. The inlet H_2S concentration was varied between 400 and 2000 ppm and the airflow rate was varied between 0.03 and 0.12 m^3/h. However, the system performance was not affected by changing the operational conditions and a maximal removal efficiency of 100% was obtained. During the experiment, the pH of the nutritive solution decreased to 2-3, but this did not affect the process performance.

Soreanu et al. (2005) developed a laboratory-scale biotrickling system in order to remove H_2S from digester biogas under anaerobic conditions. In these experiments, polypropylene balls inoculated with anaerobically digested sludge were used as packing material in the bioreactor (packing volume of 0.0062 m^3, 90% volume free). Sodium sulfite was added in the nutritive solution as an oxygen scavenging agent. Nitrate was used as electron acceptor in the absence of oxygen. Removal efficiency greater than 85 % was achieved for an H_2S inlet concentration of 500 ppm and a gas flowrate of 0.05 m^3/h. Of particular interest, inhibition of the biological process by trace amounts of O_2 was noticed when a nitrate solution was used as the sole nitrogen/nutrient source.

CONCLUSION

The above discussion shows that the preferred treatment method for H_2S gas containing streams depends on the source of the gas. In the case of H_2S in biogas, anaerobic methods involving phototrophic bacteria provide the inherent advantage of maintaining the anaerobic nature of the gas and avoid any potential safety problems. *Cholorobium limicola* is a desirable bacterium to use due to its growth using only inorganic substrates, efficiency at converting sulfide to elemental sulfur, and extracellular production of elemental sulfur. Because of the reduced requirement for separation of the biomass and the ability to achieve higher loadings, fixed-film reactors have the greatest potential for more cost-effective sulfide conversion. If light is controlled properly, the oxidation product is mostly sulfur which is non toxic and non-corrosive. Light supply is one

of the key cost components and the major constraint for this process. It is important to provide economical light energy so that the process can be established as a viable alternative to physicochemical processes currently in use. The development and use of energy efficient LEDs and the proper use of sunlight and reflectors to minimize the electrical energy use are the current research needs.

Chemotrophic bacteria require careful control of the oxygen concentration to produce elemental sulfur instead of sulfate. Even at the highest rates of conversion of sulfide to elemental sulfur, some sulfate is still produced. Bacteria of *Thiobacillus* sp. which have the ability to grow under various environmental stress conditions such as oxygen deficiency, acid conditions, etc. are widely used for the conversion of H_2S and other sulfur compounds by biological processes. The removal of H_2S using bioscrubbers involves a two stage process: absorption of H_2S by a liquid medium followed by the biological oxidation of H_2S in the liquid. Little data on the cost of plants using bioscrubbers is available, however the existence of full scale facilities of this nature are a good indication of their cost-effectiveness.

Biofiltration has also been demonstrated for the removal of H_2S from wastewater treatment plant off-gases. It is also effective in removing other volatile organic compounds present in biogases. The process is essentially aerobic and the oxidation product is mostly sulfate rather than sulfur. Drawbacks of this technology are that the sulfate can reduce the pH of the media and sulfur deposition can reduce its efficiency. However, the biofilter medium is inexpensive and may contain sufficient nutrients for the microbial communities. The process is also suitable for treating off-gases from livestock farming which contain a mixture of H_2S and NH_3. Biofiltration by aerobic bacteria is not suitable for the treatment of biogas since the presence of significant levels of oxygen in the purified gas may pose a potential safety problem.

Anaerobic biofiltration of H_2S can provide the same advantages of aerobic biofiltration including the use of low cost materials, the exclusion of aeration costs as well as the elimination of safety risks associated with operation in an oxygen-rich environment. The use of *T. denitrificans* has great potential in this respect and nitrified mixed liquor suspended solids from activated sludge/biological nutrient removal plant as suggested by Kleerebezem and Mendez (2002) can be a useful source of nitrate. Several research studies are expected in this area. A system combining the advantages of phototrohy and chemotrophy may also be considered.

Two separate biofilters employing *C. limicola* and *T. denitrificans* can be used alternatively for treating biogas from a single source. Bioreactor/filter containing phototrophic bacteria can treat hydrogen sulfide during daytime using sunlight, whereas biogas can be directed to the biofilter containing *T. denitrificans* during the night. Operational flexibility regarding sulfur recovery and filter cleaning can be achieved using this dual filter process.

Finally, for a biogas purification system, simultaneous removal of hydrogen sulfide and siloxane is required since siloxane itself can cause significant damage to combustion engines. Grumping et al. (1999) has reported anaerobic microbial degradation of siloxane. The development of an anaerobic process which is able to remove both hydrogen sulfide and siloxane simultaneously is an important current research need.

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