Chemical and biological technologies for hydrogen sulfide emission control in sewer systems: A review

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Biogenic corrosion of sewers represents a cost of about 10% of total sewage treatment cost in Flanders (Belgium) and is further increasing. In the past, research has resulted in a number of prevention methods, such as injection of air, oxygen, H$_2$O$_2$, NaClO, FeCl$_3$ and FeSO$_4$. The possibility of biological oxidation of sulfide using nitrate as the electron acceptor has also been explored in sewer systems. However, all of these methods have a problem with the high cost ($1.9\text{–}7.2\text{ kg}^{-1}\text{ S removal}$). In this review, new approaches for hydrogen sulfide emission control in sewer systems are discussed. The control of hydrogen sulfide emission by using a microbial fuel cell (MFC) can be cost-effective while the BOD is removed partially. The use of phages that target sulfate-reducing bacteria (SRB) can possibly inhibit sulfide formation. Novel inhibitors, such as slow release solid-phase oxygen (MgO$_2$/CaO$_2$) and formaldehyde, warrant further study to control hydrogen sulfide emission in sewer systems.

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1. Introduction

Hydrogen sulfide emission in sewer systems is associated with several problems, including biogenic corrosion of concrete, release of obnoxious odors to the urban atmosphere and toxicity of sulfide gas to sewer workers (ASCE, 1989; Nielsen and Keiding, 1998; Nielsen et al., 1998; US Environment Protection Agency (US EPA), 1974). Minor problems of concrete corrosion have been reported when the concentration of total sulfide in the wastewater is within the range of 0.1–0.5 mg S L\(^{-1}\). Severe concrete corrosion may occur at sulfide concentrations from 2.0 mg S L\(^{-1}\) on (Hvitved-Jacobsen et al., 2002). In Los Angeles County, approximately 10% of the sewer pipes are subject to significant sulfide corrosion, and the costs for the rehabilitation of these pipelines are roughly estimated at €400 million (Sydney et al., 1996). The restoration of the overall damaged sewer systems in Germany is estimated to cost about €100 billion per year (Kaempfer and Berndt, 1998). In Flanders (Belgium), biogenic sulfuric acid corrosion of sewers is approximated at €5 million per year, representing about 10% of total cost for wastewater collection and treatment (Vincke, 2002).

To solve the biogenic corrosion problem, several methods have been investigated, i.e. (1) optimizing the sewer hydraulic design to minimize sulfide generation, (2) sulfate source control technologies such as urine separation or pretreatment, (3) improving the resistance of sewer pipes to biogenic corrosion and (4) decreasing hydrogen sulfide emission from sewage (De Belie et al., 2004; Monteny et al., 2000, 2001; Nielsen et al., 2006a; Scrivener et al., 1999; Yamanaka et al., 2002; US EPA, 1991). This review focuses on chemical and biological technologies that prevent or decrease hydrogen sulfide emission in sewer systems (Fig. 1).

One category involves increasing redox potential, thus decreasing sulfide production. Increasing redox conditions involves addition of thermodynamically favorable electron acceptor compounds such as oxygen, nitrate or nitrite (Bentzen et al., 1995; Hobson and Yang, 2000; Londry and Sufita, 1999). Alternatively, SRB activity can also be inhibited by pH elevation or inhibitors such as biocides and molybdate (Jayaraman et al., 1999; Nemati et al., 2001c; Reinsel et al., 1996).

Another category is chemical and biological removal of sulfide (e.g. addition of iron salts, \(\text{H}_2\text{O}_2\), chlorines or nitrate) that may be considered as ultimate treatments to remove sulfide (Cadena and Peters, 1988; US EPA, 1991). Addition of iron salts or precipitation of ferrous sulfide removes dissolved sulfide from the sewage (Nielsen et al., 2005c; Padival et al., 1995; Tomar and Abdullah, 1994). Addition of \(\text{H}_2\text{O}_2\) or chlorines chemically oxidizes sulfide, thereby decreasing the amount of dissolved sulfide (Tomar and Abdullah, 1994; Waltrip and Snyder, 1985). Addition of nitrate and nitrite may also favor biological oxidation of sulfide by means of nitrate-reducing, sulfide-oxidizing bacteria (NR-SOB) (García De Lomas et al., 2005; McInerney et al., 1996; Nemati et al., 2001a,b; Shelley et al., 2005).

In recent years, significant increase in the knowledge on biological and chemical technologies for hydrogen sulfide emission control in existing sewer systems has been made. This paper summarizes the current state and explores future research possibilities.

2. Biogenic corrosion of sewer systems

2.1. Sulfur cycle in sewers and the environmental parameters

Several processes are associated with the sulfur cycle in sewer networks (Sand, 1997; Lens and Kuenen, 2001). The conceptual models for simulation of the sulfur cycle process and prediction of sulfide buildup in sewers have been developed recently (Lahav et al., 2004, 2006; Hvitved-Jacobsen et al., 1998; Matos and Aires, 1995; Nielsen et al., 2005a–c; Yongisri et al., 2003, 2004b). Fig. 2 outlines the major processes and environmental parameters associated with the sulfate cycle in sewer systems, including the bulk wastewater, biofilms, sediments, atmosphere and surface exposed to the atmosphere. These processes are (1) formation of sulfide, (2) volatilization of hydrogen sulfide, (3) chemical and biological oxidation of sulfide and (4) precipitation of metal sulfides.

For domestic wastewater, the main source of sulfur is sulfate (\(\text{SO}_4^{2-}\)) in a concentration range of 40–200 mg L\(^{-1}\) (Araujo et al., 2000; Kalogo and Verstraete, 1999; Paing et al., 2000). Sulfate can be reduced to sulfide by sulfate-reducing bacteria (SRB) (Fig. 2). This biological process mainly occurs in biofilms and sediments under anaerobic conditions in the submerged part of sewers (Beardslay et al., 1956; Carpenter, 1932; Parande et al., 2006). It is readily observed in areas with
Fig. 1 – Chemical and biological technologies for H₂S emission control in sewer systems (modified from García De Lomas et al., 2005). SRB: sulfate-reducing bacteria.

Environmental parameters

Major sulfide processes

Environmental parameters

- SOB, pH, Material of sewers
- pH, Turbulence, Temperature
- pH, Conductivity, ORP

Corrosion of sewer

Odor nuisance and health related problem

H₂S(g) in the urban atmosphere

H₂S(g) in the air phase of sewers

Air-water interface

Metal sulfides (e.g. FeS)

Sulfide species in bulk wastewater

Sulfur resources, mainly sulfate

Chemical and biological oxidation

Fig. 2 – Major sulfide processes and their effect factors associated with the sulfur cycle in the sewer system (modified from Yongsiri et al., 2003). SOB: sulfide-oxidizing bacteria; SRB: sulfate-reducing bacteria; ORP: oxidation reduction potential; DO: dissolved oxygen.
slow flow rates and insufficient reaeration potential at relatively high temperature (Hvitved-Jacobsen et al., 2000; Nielsen et al., 1992).

Hydrogen sulfide in sewage is primarily present as two sulfide species, depending on the pH (Yongsiri et al., 2003). Because the pH in sewage is about 7.0, these two species are \( H_2S(aq) \) and \( HS^- \) (Eq. (1)) (Yang et al., 2005). The \( S^2- \) species is not taken into account because of its insignificant presence even at very high pH (Eq. (2)) (Fu and Shen, 1990).

\[
\begin{align*}
H_2S(aq) & \rightarrow H^+ + HS^- , \quad pK_d \approx 7.04 , \quad (1) \\
HS^- & \rightarrow H^+ + S^{2-}, \quad pK_d \approx 11.96 , \quad (2) \\
H_2S(aq) & \rightarrow H_2S(g), \quad \kappa \approx 461 \ atm \ (mole \ fraction)^{-1} . \quad (3)
\end{align*}
\]

Only \( H_2S(aq) \) can be transferred across the air–water interface, giving rise to the emission of hydrogen sulfide from wastewater to the sewer atmosphere (Eq. (3)) (Fu and Shen, 1990) (Fig. 2). Hydrogen sulfide emission is a physico-chemical process involving both the water and air phases of sewer networks (Elmaleh et al., 1998). It is dependent on temperature, pH, hydraulic conditions of the water phase and ventilation of the air phase (Yongsiri et al., 2004a, b, 2005). Field investigations in the USA by Pomeroy and Bowlus (1946), in Australia by Thiilethwayne and Goleb (1972) and in Portugal by Matos and Aires (1995) showed clear evidence of hydrogen sulfide being present in concentrations of up to about 300 mg m\(^{-3}\) in the atmosphere of gravity sewers and sewer structures.

The main transformation and fate of hydrogen sulfide are precipitation of metal sulfides and chemical/biological oxidation (Fig. 2). The presence of metals such as iron, zinc, lead and copper in the wastewater leads to precipitation of metal sulfides and thereby decreases sulfide emission. Oxidation of sulfides in sewer networks can occur both chemically and biologically, making the total oxidation processes complex (Gadekar et al., 2006). Biological oxidation of hydrogen sulfide can take place at the sewer surfaces exposed to the sewer atmosphere. The aerobic and autotrophic Thiobacillus sp. growing on the moist surface can oxidize hydrogen sulfide to sulfuric acid (Devereux et al., 1989; Gadekar et al., 2006; Islander et al., 1991). The sulfuric acid generated will subsequently attack the sewers and their structures by reacting with corroding compounds, such as cement and metals.

### 2.2. Sewer corrosion by hydrogen sulfide emission

\[
H_2S + 2O_2 \rightarrow H_2SO_4 . \quad (4)
\]

Hydrogen sulfide in the sewer gas phase diffuses into the thin liquid film present at sewer surfaces. At the surface, chemoautotrophic bacteria will oxidize the sulfide to sulfuric acid (Eq. (4)). The corrosion process occurs by the reaction of the biogenic sulfuric acid with the cementitious material of the concrete and results in the eventual structural failure of sewers (Wiener et al., 2006). This is characterized by the production of a corroding layer on the surface of the concrete. This layer consists of gypsum (CaSO\(_4\) of various hydration states) and moisture (Mori et al., 1992). The thickness of this layer expands into the concrete, as more and more acid is produced to react with the concrete. The formation of ettringite (3CaO·Al\(_2\)O\(_3\)·CaSO\(_4\)·12H\(_2\)O or 3CaO·Al\(_2\)O\(_3\)·3CaSO\(_4\)·31H\(_2\)O) during the acid reaction process causes another facet of the problem (Redner et al., 1991, 1994). Ettringite is expansive and causes internal cracking and pitting, which provides a larger surface area for the chemical reaction to occur. This will also provide further sites of penetration of the acid into the concrete. The conversion of concrete to gypsum and ettringite weakens the structural integrity of the concrete pipe (Yamanaka et al., 2002). This decreases the load-bearing capacity of the concrete and can result in the eventual collapse of the sewer.

Table 1 presents a summary of the literature concerning the sewer corrosion rates and the lifetimes. The US EPA investigated 131 cities and 66 of them were reported to have corrosion problems. The US EPA (1991) reported that the concrete corrosion rate in sewer pipes is 2.5–10 mm year\(^{-1}\) based on the investigation of 34 cities. Other references pointed out that the average concrete corrosion rate is about 3 mm year\(^{-1}\) and that the lifetime of sewer pipes is only about 50 years (Davis et al., 1998; Ismail et al., 1993; Morton et al., 1991; Mori et al., 1992). In Belgium, severely corroded sewer pipes were examined in the district of Bruges; corrosion rates of 1.1–1.8 mm year\(^{-1}\) were observed (Vincke et al., 2002). Monteny et al. (2001) reported that a concrete corrosion rate of 1.0–1.3 mm year\(^{-1}\) was found for Portland fly ash concrete that was believed to be resistant to sulfide-oxidizing bacteria (SOB). The lifetime of Portland fly ash concrete sewer pipes was estimated to be 90–160 years.

### 3. Increasing redox potential to control sulfide formation

#### 3.1. Air or oxygen injection

Sulfide can be produced in a slime layer depth of 1 mm and more in sewers containing aerobic wastewater, because the layer containing oxygen is only 0.4 mm deep (Yu et al., 1998). If dissolved oxygen (DO) is present around the slime layer, the oxygen boundary layer containing oxygen is only 0.4 mm deep (Yu et al., 1998).

#### Table 1 – Corrosion rate and lifetime of sewer pipes

<table>
<thead>
<tr>
<th>Corrosion rate (mm year(^{-1}))</th>
<th>Lifetime(^a) (year)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5–10</td>
<td>20–70</td>
<td>US EPA (1991)</td>
</tr>
<tr>
<td>2.7</td>
<td>65</td>
<td>Morton et al. (1991)</td>
</tr>
<tr>
<td>4.3–4.7</td>
<td>35–45</td>
<td>Mori et al. (1992)</td>
</tr>
<tr>
<td>2–4</td>
<td>45–90</td>
<td>Ismail et al. (1993)</td>
</tr>
<tr>
<td>3.1</td>
<td>55</td>
<td>Davis et al. (1998)</td>
</tr>
<tr>
<td>1.0–1.3(^b)</td>
<td>130–170</td>
<td>Monteny et al. (2001)</td>
</tr>
<tr>
<td>1.1–1.8</td>
<td>90–160</td>
<td>Vincke et al. (2002)</td>
</tr>
</tbody>
</table>

\(^a\) The lifetime is the ratio of concrete sewer pipes thickness to corrosion rate. The thickness of concrete sewer pipes is 6–8 inches (1 inch = 25.4 mm) (University of Virginia, 2006).

\(^b\) The material of sewer pipes is Portland fly ash that is believed to be resistant to SOB.
as it passes into an aerobic environment (Nielsen et al., 2003, 2005b, 2006a,b). If DO is not present, dissolved sulfide will enter the bulk wastewater where it can be present as dissolved hydrogen sulfide gas (H₂S). DO levels above 0.5 mg L⁻¹ can generally prevent sulfide occurrence (US EPA, 1991). A DO level of 0.2–1.0 mg L⁻¹ at the terminal point of sewers has been reported when air injection was used to control sulfide emission (Ochi et al., 1998; Tanaka and Takenaka, 1995). Air injection is most commonly applied to force mains and wet wells (Tanaka et al., 2000). Advantages of air injection include a decrease of BOD in sewage and its nontoxicity. A disadvantage of air injection is the limited oxygen transfer (US EPA, 1992).

Because pure oxygen is five times more concentrated than air, it is possible to achieve higher DO levels (5–7 mg L⁻¹) in sewage by injecting pure oxygen instead of air (DO levels are 3–5 mg L⁻¹) (Chen and Leung, 2000; Delgado et al., 1998). Pure oxygen may therefore be a more effective method of sulfide control for cases where the total oxygen requirement exceeds that which can be transferred using air injection. Use of pure oxygen as a sulfide control method is particularly advantageous in a pressurized sewer system, because dissolution of oxygen is greater at higher pressures. The disadvantages are that it is applicable only to the high-pressure force mains and that it represents fire risks (US EPA, 1992).

### 3.2. Addition of nitrate

The preventive effect of nitrate on sulfide production has been reported (Allen, 1949; Yang et al., 2005). Both transient and long-term preventions of sulfide production have been found (Allen, 1949; Beardslay et al., 1956; Carpenter, 1932; Heukelelekian, 1943; Poduska and Anderson, 1981). Carpenter (1932) reported that sodium nitrate was used to control odor nuisance. Heukelelekian (1943) observed that in oxygen-deficient systems, nitrate was reduced preferentially over sulfate, thus diminishing H₂S formation. Allen (1949) found that the addition of 1.0 g L⁻¹ of nitrate to sewage sludge prevented sulfide production for at least 29 days. This prevention was attributed to the increase in redox potential caused by the presence of nitrate. Poduska and Anderson (1981) showed that nitrate addition could control sulfide generation in a wastewater lagoon as long as enough nitrate was added initially to raise the redox potential of the lagoon above 300 mV. The addition of nitrate as a biological oxidation strategy by means of NR-SOB will be discussed in Section 6.

### 4. Inhibition of SRB activity

Considering inhibition of biological activity, pH elevation is the most common method, but other inhibitors (e.g. biocides and molybdate) have also been considered (Jayaraman et al., 1999; Nemati et al., 2001c; Reinsel et al., 1996). At a pH above 9.0, the amount of H₂S(SO₄) in solution is negligible since the sulfide present is nearly entirely in its ionic form (HS⁻) (Eq. (1)). However, continuous feeding of sodium hydroxide (NaOH) to maintain an elevated pH (more than 9) is expensive and may disrupt downstream treatment processes. The most effective use of sodium hydroxide is shock treatment to produce a pH of 12.5–13.0 in wastewater for a period of 20–30 min (US EPA, 1991). Such a high pH inactivates SRB in the slime layer for a period of a few days to 2 weeks. The wastewater of the high pH section has to be isolated at the wastewater treatment plant (WWTP) and fed slowly into the system if it is not diluted in the collection system (US EPA, 1991).

### 5. Chemical removal of sulfide

#### 5.1. Precipitation by metal salts

**5.1.1. Insoluble metal sulfides in sewage**

Precipitation of metal sulfides removes dissolved sulfide from the wastewater, thereby decreasing the amount of sulfide available for release to the sewer atmosphere. At conditions of low or moderate sulfide concentrations in the wastewater, a significant fraction of the total amount of sulfide may be present as insoluble metal (e.g. ferrous, zinc, copper, nickel and manganese) sulfides (Nielsen et al., 2005a,b). Field investigations conducted by the Brisbane City Council in 1980 demonstrated the importance of metal sulfide precipitation for the sulfur cycle (ASCE, 1989). This study showed that generally no dissolved sulfide was present when the total sulfide concentration was approximately 0.12 mg S L⁻¹. Precipitation with metals present in the wastewater is therefore believed to play a central role in controlling the dissolved sulfide concentration and the extent of associated problems.

**5.1.2. Addition of iron salts**

Iron is typically one of the dominant metals present in municipal wastewater. The concentration level of iron, which is typically 0.4–1.5 mg L⁻¹, suggests the formation of iron sulfide to be an important process of the sulfur cycle in wastewater (Henze et al., 1997; Nielsen et al., 2005b). Because of its effectiveness in controlling the dissolved sulfide concentration, iron has been widely used to control sulfide buildup in sewer networks (ASCE, 1989; Hvitved-Jacobsen et al., 2002; Jameel, 1989). Iron salts of chloride (Jameel, 1989; Nielsen et al., 2005a,b), sulfate (US EPA, 1974) or nitrate (Padival et al., 1995) have been added to wastewater either in ferric or ferrous forms. Fe (II) can remove sulfide by precipitation as ferrous sulfide (FeS) according to Eq. (5). Fe (III) can remove sulfide by oxidizing it chemically to elemental sulfur while being reduced to Fe (II), which can subsequently produce FeS (Eqs. (5) and (6)).

\[
2Fe³⁺ + HS⁻ \rightarrow FeS + H⁺, \quad AG : \quad -21.0 \text{kJ mol}⁻¹ \quad (\text{HS}⁻). \tag{5}
\]

\[
2Fe²⁺ + HS⁻ \rightarrow 2Fe²⁺ + S⁰ + H⁺, \quad AG : \quad -160.9 \text{kJ mol}⁻¹ \quad (\text{HS}⁻). \tag{6}
\]

The precipitation of ferrous sulfide in wastewater is believed to be a rapid process. However, Nielsen et al. (2005a) found that iron sulfide precipitation in anaerobic wastewater spiked with ferric chloride could take a few hours. The formation of iron phosphate and complexation of iron by ligands (e.g. EDTA) can compete with the formation of iron sulfide in wastewater (Araújo et al., 2000; Nielsen et al., 2005a). Further investigation is needed to explore the sulfur...
and phosphorus transformation and the effect of iron byligands (e.g. EDTA) on formation of iron sulfide in sewers. Whether ferrous or ferric ion is more effective in controlling the dissolved sulfide concentration remains controversial from the literature. Jameel (1989) reported ferrous chloride to be more than twice as effective in controlling the dissolved sulfide concentration compared to ferric chloride. In contrast, Tomar and Abdullah (1994) reported a ferric salt solution to be slightly more effective than a ferrous salt solution, i.e. the iron dosage for complete sulfide control was 20% lower for the ferric salt solution than the ferrous salt solution. Field studies however indicated that a mixture of ferrous and ferric iron salts is most effective in controlling the dissolved sulfide concentration (Padival et al., 1995; US EPA, 1974). They also showed that despite the very low solubility of iron sulfide, complete control of dissolved sulfide is difficult and that iron salts must be added in excess to obtain adequate control. In practice, it is difficult to decrease the dissolved sulfide concentration to less than 0.2 mg L\(^{-1}\) (ASCE, 1989).

5.1.3. Operation conditions and costs

Table 2 presents a summary of the literature concerning the use of iron salts for hydrogen sulfide precipitation. The proper ratio of iron to sulfide is 1.2–2.5:1 (w/w) and average eliminations of 88–100% have been found (Nielsen et al., 2005a; Padival et al., 1995; Tomar and Abdullah, 1994). The range in cost is £3.7–7.2 kg\(^{-1}\) S. The costs are dependent on sulfide removal, dosage of chemicals and current prices of the chemicals. In Table 2, the costs are calculated from the ratio of chemicals to sulfide multiplied with the current price of the chemicals.

5.2. Addition of oxidizing chemicals

5.2.1. Hydrogen peroxide

When hydrogen peroxide (H\(_2\)O\(_2\)) is added to wastewater, it oxidizes dissolved sulfide and decomposes to water and oxygen, thus keeping conditions aerobic. The proper ratio of H\(_2\)O\(_2\) is 1.3–4.0 mg H\(_2\)O\(_2\) L\(^{-1}\) to 1 mg S L\(^{-1}\) and average elimination of sulfide is 85–100% (Table 2). The disadvantage is the short lifetime of H\(_2\)O\(_2\) (less than 90 min) (US EPA 1991). Therefore, it may be necessary to add the chemical at several points along the sewers.

5.2.2. Chlorine

Chlorine will oxidize sulfide to sulfate or to elemental sulfur, depending on the pH (US EPA, 1992). Its effectiveness is

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Ratio of chemicals to S (w/w)</th>
<th>Scale and volume of reactor</th>
<th>Sulfide concentration in upstream (mg S L(^{-1}))</th>
<th>Average elimination (%) of sulfide</th>
<th>Cost(^b) (£ kg(^{-1}) S)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeCl(_2) (4)H(_2)O</td>
<td>6.0–7.0:1</td>
<td>Plant scale, 59,000 m(^3)</td>
<td>More than 4.0</td>
<td>90</td>
<td>22.4–26.1</td>
<td>US EPA (1992)</td>
</tr>
<tr>
<td>FeSO(_4) (7)H(_2)O</td>
<td>1.7:1</td>
<td>Plant scale, 25,000 m(^3) d(^{-1})</td>
<td>18.0–25.0</td>
<td>95–97</td>
<td>4.8</td>
<td>Tomar and Abdullah (1994)</td>
</tr>
<tr>
<td>FeCl(_2) (_4)</td>
<td>1.2:1</td>
<td>Plant scale, 25,000 m(^3) d(^{-1})</td>
<td>18.0–25.0</td>
<td>88–98</td>
<td>4.5</td>
<td>Tomar and Abdullah (1994)</td>
</tr>
<tr>
<td>FeCl(_2) and FeCl(_3)</td>
<td>2.5:1</td>
<td>Plant scale, 75,000 m(^3) d(^{-1})</td>
<td>6.4</td>
<td>97</td>
<td>7.2</td>
<td>Padival et al. (1995)</td>
</tr>
<tr>
<td>FeCl(_3)</td>
<td>1.5:1</td>
<td>Lab scale, 3.00 L</td>
<td>3.8</td>
<td>100</td>
<td>3.7</td>
<td>Nielsen et al. (2005c)</td>
</tr>
<tr>
<td>H(_2)O(_2)</td>
<td>4.0:1</td>
<td>Plant scale, 76,000 m(^3) d(^{-1})</td>
<td>15.0</td>
<td>85–90</td>
<td>10.6</td>
<td>Waltrip and Snyder (1985)</td>
</tr>
<tr>
<td>H(_2)O(_2)</td>
<td>1.5–1.6:1</td>
<td>Plant scale, 2000 m(^3) c</td>
<td>8.5</td>
<td>90–95</td>
<td>4.0–4.2</td>
<td>US EPA (1991)</td>
</tr>
<tr>
<td>H(_2)O(_2)</td>
<td>1.3:1</td>
<td>Plant scale, 25,000 m(^3) d(^{-1})</td>
<td>20.0</td>
<td>87–100</td>
<td>3.5</td>
<td>Tomar and Abdullah (1994)</td>
</tr>
<tr>
<td>Cl(_2)</td>
<td>9.0:1</td>
<td>Plant scale, 90,000 m(^3) d(^{-1})</td>
<td>18.0</td>
<td>100</td>
<td>2.7</td>
<td>Waltrip and Snyder (1985)</td>
</tr>
<tr>
<td>Cl(_2)</td>
<td>10.0–15.0:1</td>
<td>Plant scale, 25,000 m(^3) d(^{-1})</td>
<td>–</td>
<td>–</td>
<td>2.8–4.2</td>
<td>US EPA (1991)</td>
</tr>
<tr>
<td>NaClO</td>
<td>2.0:1</td>
<td>Plant scale, 25,000 m(^3) d(^{-1})</td>
<td>20.0</td>
<td>96–100</td>
<td>2.6</td>
<td>Tomar and Abdullah (1994)</td>
</tr>
<tr>
<td>Ca(ClO(_2))(_2)</td>
<td>1.8:1</td>
<td>Plant scale, 25,000 m(^3) d(^{-1})</td>
<td>20.0</td>
<td>93–100</td>
<td>1.9</td>
<td>Tomar and Abdullah (1994)</td>
</tr>
<tr>
<td>NaClO and NaOH(^d)</td>
<td>1.0:1</td>
<td>Plant scale, 25,000 m(^3) d(^{-1})</td>
<td>18.2</td>
<td>100</td>
<td>1.9</td>
<td>Tomar and Abdullah (1994)</td>
</tr>
<tr>
<td>KMnO(_4)</td>
<td>6.0–7.0:1</td>
<td>Lab scale, 0.05 L</td>
<td>–</td>
<td>–</td>
<td>18.9–22.0</td>
<td>US EPA (1991)</td>
</tr>
<tr>
<td>NaNO(_3)</td>
<td>6.7:1</td>
<td>Lab scale, 1.37 L</td>
<td>54.0</td>
<td>100</td>
<td>12.2</td>
<td>Jenneman et al. (1986)</td>
</tr>
<tr>
<td>NaNO(_3)</td>
<td>0.18:1</td>
<td>Lab scale, 1.37 L</td>
<td>35.0</td>
<td>65</td>
<td>0.4</td>
<td>Okabe et al., (2003a)</td>
</tr>
</tbody>
</table>
frequently low because of its reactions with other components in sewage. It may be added as an aqueous solution (e.g. sodium hypochlorite) or directly as a gas. The chemical oxidation reaction is slower at lower sulfide concentrations, particularly below 1 mg L$^{-1}$. Added directly as a gas, a ratio of 9.0–15.0:1 (w/w) is suggested (Tomar and Abdullah, 1994; US EPA, 1991). Added as an aqueous solution (NaClO or Ca(ClO)$_2$), the proper ratio of chemicals to sulfide is 1.8–2.0:1 (w/w) (EPA, 1991). Added as an aqueous solution (NaClO or Ca(ClO)$_2$), 9.0–15.0:1 (w/w) is suggested (Tomar and Abdullah, 1994; US EPA, 1991).

5.3. Potassium permanganate
Potassium permanganate (KMnO$_4$) is a strong oxidizing agent, which converts sulfide to sulfate. It is normally supplied in a dry state, but is fed as a 6% solution in water (US EPA, 1991). The disadvantage is the high cost (€18.9–22.0 kg$^{-1}$ S) (Table 2). The costs for H$_2$O$_2$ and chlorine are in the range of €1.9–4.2 kg$^{-1}$ S (Table 2).

6. Biological oxidation of sulfide

Recently, it has been shown that sulfide emission control after addition of nitrate can be explained by the action of NR-SOB oxidizing the H$_2$S produced by the SRB. Some studies have been carried out in oil reservoir environments (Myhr et al., 2002; Nemati et al., 2001a, b), and in sewage environments (Æsøy et al., 2002; Bentzen et al., 1995; Jenneman et al., 1986; Jobbagy et al., 1994; Okabe et al., 1999, 2003a, b). Most experiments have been conducted using pure cultures of SRB (Jenneman et al., 1986; Nemati et al., 2001a, b). Some experiments have been done at pilot (Hobson and Yang, 2000) or plant scale (Bentzen et al., 1995; Einarsen et al., 2000; Moody and Riek, 1999; Garcia De Lomas et al., 2005). Studies performed on oil reservoirs have pointed out the highly significant role of NR-SOB as important components of the microbial communities in experimental research on the inhibition of sulfide production by addition of nitrate (Jenneman et al., 1986; Nemati et al., 2001b). Among the microorganisms suspected to play a critical role in these processes, Thiomicrospira denitrificans, an e-Proteobacterium, and Thiothrix denitrificans, a b-Proteobacterium, have been reported (Kodama and Watanabe, 2003; Voordouw et al., 1996). These two bacterial species are only able to oxidize sulfides in the presence of nitrate, of which the reduction is associated with the oxidation of sulfides and sulfur (Kelly et al., 1997; Kodama and Watanabe, 2003). Anoxic sulfide oxidation with nitrate as the electron acceptor was also observed in the presence of Beggiatoa enrichment (Anja et al., 2006). Sayama et al. (2005) demonstrated that marine Beggiatoa oxidizes HS$^-$/S$^0$, which can be stored as intracellular globules, and subsequently to SO$_4^{2-}$. Buisman et al. (1990) demonstrated that S$^0$ accumulates as end product in a biological oxidation reactor when O$_2$ is the electron acceptor. Gadkar et al. (2006) demonstrated that S$^0$ accumulates as product in oil reservoir environments when NO$_3$ is the electron acceptor. For the sewage environment, Nielsen et al. (2005c) and Yang et al. (2005) discussed the process kinetics of biological sulfide oxidation in wastewater and

### Table 2 (continued)

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Ratio of chemicals to S (w/w)$^a$</th>
<th>Scale and volume of reactor</th>
<th>Sulfide concentration in upstream (mg L$^{-1}$)</th>
<th>Average elimination (%) of sulfide</th>
<th>Cost$^b$ (€ kg$^{-1}$ S)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaNO$_3$</td>
<td>1.37:1</td>
<td>Lab scale, 1.00 L</td>
<td>10.2</td>
<td>100</td>
<td>2.5</td>
<td>Okabe et al. (2003b)</td>
</tr>
<tr>
<td>NaNO$_3$</td>
<td>1.4–4.6:1</td>
<td>Lab scale, 3.00 L</td>
<td>2.5–3.5</td>
<td>90–95</td>
<td>2.5–8.3</td>
<td>Yang et al. (2005)</td>
</tr>
<tr>
<td>Nutriox$^{TM}$</td>
<td>0.88:1</td>
<td>Plant scale, 3700 m$^3$ d$^{-1}$</td>
<td>5.1</td>
<td>63–95</td>
<td>2.1</td>
<td>Bentzen et al. (1995)</td>
</tr>
<tr>
<td>Nutriox$^{TM}$</td>
<td>0.60:1</td>
<td>Pilot scale, 200 L</td>
<td>9.6</td>
<td>95</td>
<td>1.5</td>
<td>Hobson and Yang (2000)</td>
</tr>
<tr>
<td>Nutriox$^{TM}$</td>
<td>2.50:1</td>
<td>Plant scale, 15,000 m$^3$ d$^{-1}$</td>
<td>70.0</td>
<td>95–100</td>
<td>6.0</td>
<td>Einarsen et al. (2000)</td>
</tr>
<tr>
<td>Nutriox$^{TM}$</td>
<td>0.36:1</td>
<td>Plant scale, 50,000 m$^3$ d$^{-1}$</td>
<td>70.0</td>
<td>68–95</td>
<td>0.9</td>
<td>Garcia De Lomas et al. (2005)</td>
</tr>
<tr>
<td>Ca(NO$_3$)$_2$</td>
<td>1.92:1</td>
<td>Plant scale, 2000 m$^3$ d$^{-1}$</td>
<td>2.6</td>
<td>4.4</td>
<td>1.5</td>
<td>Rodriguez-Gomez et al. (2005)</td>
</tr>
</tbody>
</table>

$^a$ For the iron salts, it is the ratio of Fe to S (w/w); for the nitrate salts, it is the ratio of NO$_3^-$:N to S (w/w); for other chemicals, it is the ratio of chemical to S (w/w).

$^b$ The prices of chemicals are provided by Brenntag NV Co. Ltd., VWR Inc., Belgium, Wuhan industrial Co. Ltd., China and Yara Industrial Limited, Ireland.

$^c$ The total volume of sewer pipes.

$^d$ The ratio of FeCl$_3$ to FeCl$_2$ is 1.9:1. The ratio of NaClO to NaOH is 3.5:1.

$^e$ Nutriox$^{TM}$ is the concentrated calcium nitrate, a commercially available solution of 8.8% NO$_3$ in 0.88:1 Plant scale.

### References

- Buisman et al. (1990)
- Kelly et al. (1997)
- Kodama and Watanabe (2003)
- Voordouw et al. (1996)
- Sayama et al. (2005)
- Anja et al. (2006)
hypothesized that $S^0$ can be an important end-product under anoxic conditions when $O_2$ or $NO_3^-$ is the electron acceptor (Eqs. (7) and (8)). Formation of sulfate was observed as soon as the sulfide concentration reached a negligible level (Eqs. (9) and (10)). When $NO_3^-$ is used as the electron acceptor, the oxidation of $HS^-$ to $S^0$ increases the pH, while the oxidation of $S^0$ to $SO_4^{2-}$ decreases the pH (Eqs. (7)–(10)) (Gadekar et al., 2006).

$$\text{HS}^- + \text{NO}_3^- + \text{H}^+ \rightarrow S^0 + \text{NO}_2^- + \text{H}_2\text{O}. \quad (7)$$

$$\text{HS}^- + 0.4\text{NO}_3^- + 1.4\text{H}^+ \rightarrow S^0 + 0.2\text{N}_2 + 1.2\text{H}_2\text{O}. \quad (8)$$

$$S^0 + 3\text{NO}_3^- + \text{H}_2\text{O} + 3\text{H}^+ \rightarrow \text{SO}_4^{2-} + 3\text{NO}_2^- + 5\text{H}^+. \quad (9)$$

$$S^0 + 1.2\text{NO}_3^- + 0.4\text{H}_2\text{O} + 1.2\text{H}^+ \rightarrow \text{SO}_4^{2-} + 0.6\text{N}_2 + 2\text{H}^+. \quad (10)$$

The theoretical nitrate demand for sulfide oxidation to sulfur is estimated to be 0.18–0.44 mg NO$_3^-$-N (mg S)$^{-1}$ (Yang et al., 2005). However, the dosages varied with the nature and concentration of organic matter, biomass activity and ionic strength in the different sewages (Luis et al., 2005). The stoichiometry reported in most literature ranged from 0.6 to 4.5 mg NO$_3^-$-N (mg S)$^{-1}$, with an average sulfide elimination of 90–100% (Table 2). Okabe et al. (2003a), and Garcia De Lomas et al. (2005) reported a nitrate demand of 0.18–0.36 mg NO$_3^-$-N (mg S)$^{-1}$, with an average sulfide elimination of 65–95%. The range in cost is €1.5–8.3 kg$^{-1}$$\text{S}$ and the average cost in the literature is about €2.1–2.5 kg$^{-1}$$\text{S}$.

7. Outlooks

7.1. Formaldehyde or para formaldehyde

It was reported that inhibitors such as molybdate can be used to control hydrogen sulfide emission in sewer systems (Nemati et al., 2001c). Formaldehyde is widely used as an inhibitor of bacteria, even in food producing processes such as aquaculture, while it can be biodegraded in WWTPs (Heck et al., 2001; Kajitvichyanukul and Suntronvipart, 2006; Pedersen et al., 2007; Pedersen and Pedersen, 2006). Paraformaldehyde ($n = 8–100$) is a cheap and chemical and is used as an alternative for formaldehyde in many industrial applications (Helander, 2000). Parafomaldehyde is converted into formaldehyde at room temperature at neutral pH in aqueous solutions (McMurry, 2003). It is worthwhile to explore whether formaldehyde and paraformaldehyde could be used to lower hydrogen sulfide generation in sewers (Fig. 3). A preliminary investigation has shown that a formaldehyde concentration of 10–20 mg L$^{-1}$ was sufficient to inhibit hydrogen sulfide generation in the sewage (Zhang et al., unpublished results). Formaldehyde is readily soluble in water and reacts substantially and reversibly with water to form methanediol [CH$_2$(OH)$_2$] (Seyfoglu and Odabasi, 2007). Moreover, the sewer systems are closed so the exchange between urban atmosphere and gas phase in sewer systems is limited. Toxicity to sewer workers is another concern when formaldehyde or paraformaldehyde is used as an inhibitor. Formaldehyde is commonly used to treat external fish parasites and fungal diseases (Pedersen and Pedersen, 2006; Pedersen et al., 2007). Concentrations frequently used are 25–40 mg L$^{-1}$ formaldehyde as an indefinite bath treatment or 250 mg L$^{-1}$ formaldehyde for a 1-h bath (Wooster et al., 2005). In our preliminary investigation, 10–20 mg L$^{-1}$ formaldehyde was found as the optimum dosage to control sulfide generation in sewage. With protection equipment, the operation environment thus should be acceptable for sewer workers. However, further study is necessary to investigate the risk of formaldehyde to both the urban environment and the health of sewer workers.

The price of formalin (36–40% formaldehyde) is €59 (100 kg)$^{-1}$ (Brenntag NV, Belgium). The range in cost for this method, €1.3–3.6 kg$^{-1}$ S removal, is in the same range as the biological oxidation technology (€2.1–2.5 kg$^{-1}$ S removal).

7.2. Slow release solid-phase oxygen (MgO$_2$/CaO$_2$)

For oil wells and river sediments, many different technologies have been developed, which have never been used in hydrogen sulfide emission control in sewer systems. Lee et al. (2005) reported the use of slow release solid-phase oxygen, such as magnesium peroxide (MgO$_2$) and calcium peroxide (CaO$_2$), injected to sediments of lakes or rivers to inhibit anaerobic biological activity. They react with water to release oxygen slowly to produce magnesium hydroxide and calcium hydroxide (Mg(OH)$_2$ and Ca(OH)$_2$). Chemical oxidation of sulfide and biotic inhibition of SRB are two major mechanisms by which slow release solid-phase oxygen may be able to decrease sulfide concentration in water (Chang et al., 2007). After a series of lab-scale batch tests, 0.4% MgO$_2$ was found to be able to inhibit the formation of H$_2$S for more than 40 days in an SRB-enriched environment (Chang et al., 2007). By providing long-term inhibition of the SRB activity, slow release solid-phase oxygen provides a good alternative means of controlling the generation of H$_2$S in water. It might be interesting to evaluate the effectiveness and economic possibility of these oxidizers to control hydrogen sulfide emission in sewer systems (Fig. 3). The challenge is how to make the solid-phase oxygen stay in the sewers without being flushed away. The fate of such products under normal dry weather conditions should be sufficiently high to guarantee full effect.

7.3. Microbial fuel cells (MFCs)

A fuel cell is an electrochemical device that continuously converts chemical energy to electrical energy for as long as...
fuel and oxidant are supplied to it. Several researchers have demonstrated the use of hydrogen sulfide as a fuel in a solid oxide fuel cell (Aguilar et al., 2004; Kirk and Winnick, 1993; Peterson and Winnick, 1996). Microbial fuel cells (MFCs) are devices capable of directly transforming chemical to electrical energy by electrochemical reactions involving biochemical pathways. MFCs function on different carbohydrates but also on complex substrates present in wastewaters. In the last 10 years, scientists devoted a lot of research and development concerning MFCs. Rabaey et al. (2006) reported that dissolved sulfide can be converted to elemental sulfur by MFCs. Sulfide oxidation in the anodic compartment resulted in electricity generation with power outputs up to 101 mW L⁻¹ net anodic compartment. The MFCs were connected with an upflow anaerobic sludge reactor, providing removal of up to 98% and 46% of the sulfide and acetate, respectively. It might be interesting to control hydrogen sulfide emission by using a MFC in sewer systems (Fig. 3). Sulfide can be oxidized when it functions as a mobile carrier of electrons from bacteria to electron acceptors. A scheme of a possible design of a MFC in sewer systems is shown in Fig. 4. If the device can be successfully developed, it should be cost-effective while the formed sulfur can be precipitated and potentially harvested (Krishnakumar et al., 2005). The concomitant electricity generation can be an additional advantage.

7.4 Phages

The first phage was isolated in 1947, and since that time over 250 of these viruses have been identified (McNerney, 1999). Phages have made a significant contribution to our knowledge of bacteria (McNerney, 1999). It has been reported that phages can be technically used to kill bacteria, e.g. Escherichia coli, Enterobacter aerogenes (Randerson, 2003; Verthé and Verstraete, 2006; Verthé et al., 2004). Randerson (2003) reported that phages could help eliminate the putative pathogenic bacteria in farm animals, greatly lowering the chance of human infections. The phage decreased numbers of the unwanted bacterium by 99% in just 2 days. Verthé and Verstraete (2006) and Verthé et al. (2004) assessed phage-mediated removal of Enterobacter aerogenes under varying conditions of temperature and nutrient availability. It has been reported that phages are far more discriminating than antibiotics (Randerson, 2003). Also, the numbers of the phage rise exponentially as long as there are host bacteria left to infect. The phages continue to replicate in a harmless E. coli strain after all the target bacteria have been destroyed. Finally, while bacteria can develop resistance as they do to antibiotics, the phage can out-evolve them. The question arises whether one could find the phages that can lyse SRB efficiently (Fig. 3). If so, the method could possibly be cost-effective because the phages may reproduce in sewer systems where the hosts or co-hosts, SRB or E. coli, respectively, are present. However, one will have to show that the phage will not have an adverse effect on bacteria in activated sludge systems, receiving water bodies, soil and human gut microbiota if they happen to be passed to people via water.

8. Summary and conclusions

The main problem of current hydrogen sulfide emission control technologies is the cost (£1.9–7.2 kg⁻¹ S removal). A cost-effective and efficient method is needed to control hydrogen sulfide emission in sewer systems. This review...
provides some new points that might be helpful for future research, e.g., applications of formaldehyde, MgO2/CaO2, MFCs and phages. Formaldehyde is a cost-effective chemical (€1.3–3.6 kg−1 S removal) to inhibit the sulfide generation in sewers. Solid-phase oxygen is interesting because it can provide long-term inhibition of SRB activity. For the sewer MFCs, concomitant electricity can be generated while sulfide occurrence can be prevented. The phages that can lyse SRB efficiently could be cost-effective because they may reproduce in sewers.

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