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A laboratory assessment of the impact of brewery wastewater discharge on sulfide and methane production in a sewer

Gatut Sudarjanto, Keshab R. Sharma, Oriol Gutierrez and Zhiguo Yuan

ABSTRACT

The impact of brewery wastewater discharge on sulfide and methane production in a sewer was assessed. Experiments were carried out on laboratory scale sewer reactors consisting of both an experimental and a control reactor. The control reactor was intermittently fed with real fresh sewage while the experimental reactor was fed with a mixture of brewery and domestic wastewater at two different proportions (10 and 25% v/v). 10% v/v discharge of brewery wastewater increased the H_2S and CH_4 production rates in the sewer reactor by 40% and 30%, respectively. When the brewery wastewater fraction was increased to 25% v/v, the H_2S production rate of the experimental reactor decreased to the level of the control reactor. In contrast, the CH_4 production rate maintained at a level that was 30% higher than that in the control reactor. These results indicate that the discharge of brewery wastewater into sewers can give negative impacts in relation to odour and corrosion management of the systems and will increase the greenhouse gas emissions from sewers. The study also reveals that the impact of trade waste on the biological reactions in sewers is complex, and requires careful experimental assessment in each case.

Key words | brewery wastewater, sewer, sulfide and methane production

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INTRODUCTION

The sewer network is known as a complex system where physical, biological and chemical transformations occur and interact simultaneously before wastewater reaches the treatment plant (Thistlethwayte 1972; Hvitved-Jacobsen 2002; Zhang et al. 2008). A major problem in sewer systems, causing serious concern for wastewater authorities is the emission of hydrogen sulfide gas (H_2S) (Pomeroy 1959; USEPA 1974; Boon 1995; Hvitved-Jacobsen 2002). The gas is formed due to the reduction of oxidized sulfur species, particularly sulfate, by sulfate reducing bacteria (SRB). The release of sulfide gas causes biogenic corrosion of concrete that leads to damage of sewer infrastructures, obnoxious odour problems and also health problems to sewer workers (Thistlethwayte 1972; USEPA 1974; Nielsen & Hvitved-Jacobsen 1988; Hvitved-Jacobsen 2002). The anaerobic-dominated condition of the sewer also may cause the production of methane, which is a potent greenhouse gas and explosive at low concentrations (Spencer et al. 2006; Guisasola et al. 2008; Foley et al. 2010). Much

of the methane produced in sewer systems will likely be released to the atmosphere in gravity sections of sewers or at a wastewater treatment plant (Guisasola et al. 2008). This is because methane oxidation is a slow process, and the consumption of methane in sewers and in wastewater treatment plants is yet to be established. Where methane formation is significant, it also consumes valuable COD (Chemical Oxygen Demand) required for biological nutrient removal at the downstream wastewater treatment plant.

The discharge of trade wastewater into a sewer system is common in many countries. However, the disposal needs an approval from authorities operating sewer networks and treatment facilities. In some cases, trade wastewater may contain a high concentration of pollutants that could create detrimental environmental and economic effects in sewer systems including accelerated corrosion and increased emissions of odorous and other gases. To date, research on the impact of trade wastewater on sulfide and methane formation in sewers is still rare. In this study,

brewery wastewater is used as representative of a class of trade wastewater, that is, wastewater containing high concentrations of easily biodegradable carbon (high in carbohydrate), but low levels of proteins and also a low sulfur content.

The brewing sector has an important economic position in the food industry. Beer is a fermented beverage and recognized as a popular drink in the world with the average annual consumption around 23 L per person and becomes one of the most consumed drinks following tea, carbonates, milk and coffee (Fillaudeau *et al.* 2006; FAO 2009). Owing to the use of significant water in the process, a high volume of wastewater is generated from the brewery industry (Connaughton *et al.* 2006; Baloch *et al.* 2007). The ratios of water : beer : wastewater for each m^3 of beer produced are 4–11 : 1 : 2–8 m^3 (Driessen & Vereijken 2003). Brewery wastewaters have high biodegradability with Biochemical Oxygen Demand (BOD_5)/COD >0.5 (Driessen & Vereijken 2003; Shao *et al.* 2008) and are classified as medium-to-high-strength organic wastewater (Parawira *et al.* 2005). In general, dissolved carbohydrates, alcohol from beer wastes, suspended organic solids, (e.g. spent maize, malt, and yeast) contribute substantially to the high organic loads in the brewery wastewaters (Parawira *et al.* 2005). The wastewater is usually produced from cooling, fermentation units, and washing/cleaning of tanks and floors (Parawira *et al.* 2005; Feng *et al.* 2008; Janhom *et al.* 2009). These effluents are typically non-toxic due to the fact that dissolved organic matter usually consists of sugar, starch and protein (Speece 1996).

This study aims to experimentally assess the impacts of brewery wastewater discharge on sewers in regard to sulfide and methane formation. Continuous and batch tests of a lab scale sewer system fed with sewage and the mixture of sewage and brewery wastewater were performed to obtain more understanding on sulfide and methane production in such systems.

MATERIAL AND METHODS

Lab test set-up and procedures

Two laboratory sewer biofilm reactors were used in this study to simulate a real rising main sewer system in terms of operation and performance, one of which was used as the experimental system (R1) and other a control (R2). Each reactor had a volume of 1 L and was made of Perspex™, an acrylic polyvinyl chloride sheet, and airtight sealed to prevent any vacuum and oxygen entry during wastewater

displacement. The reactors were fully covered with aluminium foil to avoid exposing the reactor and the biofilm on reactor wall to light. Figure 1 shows the introduction of wastewater from the bottom of the reactors through a cross-shaped distributor to provide a uniform distribution. The wastewater left the system from an overflowing outlet on the top lid of the reactor. The reactors were maintained under quiescent conditions except during pumping events when the wastewater was mixed, similar to that in a real rising main. Gentle mixing was continuously provided to the reactors through a magnetic stirrer (Heindolph Model MR 3000R) operated at 240 rpm (Gutierrez *et al.* 2009).

The control reactor was intermittently fed with real fresh sewage while the experimental reactor was intermittently fed with a mixture of brewery and domestic wastewater at two different proportions (10 and 25% v/v, respectively). A peristaltic pump (Materflex model 7520-47) was used to feed wastewater into the reactors. Each reactor system was exposed to 4 pump events on a daily basis with a hydraulic retention time (HRT) of 6 h. The pH in both reactors was monitored using a pH probe with a TPS miniCHEM process monitor and controller (Version 2.1.1).

Raw sewage was collected weekly from the Robertson Park Pumping Station (Indooroopilly, Brisbane), by means of a Masterflex peristaltic pump (model 7520-47) and transported to the laboratory immediately. The brewery wastewater was collected from the Yatala Brewery Industry (Foster's Group). Both wastewaters were stored at 4 °C to minimize biological transformations, and heated to 20 °C before being pumped into the reactors (Gutierrez *et al.* 2009). Table 1 shows the characteristics of the two types of wastewater.

The study consisted of three phases as shown in Table 2. The reactors were operated for 4 months to develop mature
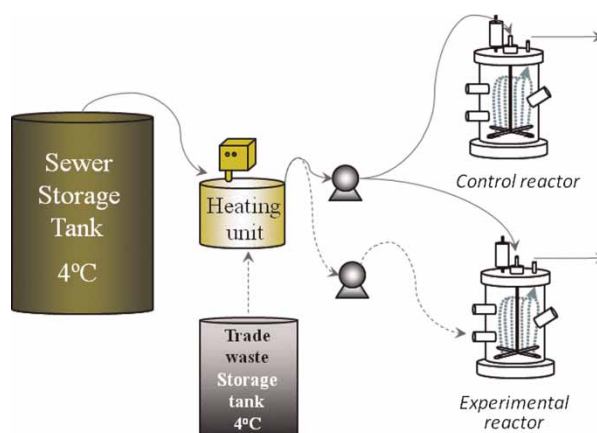

Figure 1 | Schematic of the laboratory reactor system.

Table 1 │ Typical composition of wastewaters

Parameter	Unit	Composition of feed	
		Raw sewage	Brewery wastewater
TCOD	mg COD/L	270–485	5,000–7,000
SCOD	mg COD/L	170–310	3,000–6,000
VFA	mg COD/L	50–120	250–500
Sulfate	mg S/L	10–25	10–20
Sulfide	mg S/L	<4	0
pH	–	7.2 ± 0.2	4.0 ± 0.6

Table 2 │ Details of the operational periods

Phase	Period	Composition of feed	
		Experimental reactor	Control reactor
1	23rd May–12th Nov 2008	100% domestic wastewater	100% domestic wastewater
2	27th Nov 2008–24th Feb 2009	90% domestic + 10% brewery wastewater	100% domestic wastewater
3	10th March–29th April 2009	75% domestic + 25% brewery wastewater	100% domestic wastewater

anaerobic biofilm on reactor walls and to establish pseudo-steady-state conditions. This was followed by the addition of brewery wastewater to the experimental reactor at 10% for three months. In the last 1.5 month, the brewery wastewater fraction was increased to 25%.

Batch tests were performed in each phase to observe any changes in the sulfate reduction and methane production capabilities of the sewer biofilm. In each test, the continuous operation of the reactor was temporarily halted for the duration of each batch test. The experiments were carried out immediately after fresh sewage was pumped into the reactor for 6 min to replace the whole content of the reactor (3 times replacements). Liquid samples were drawn at a regular interval (30 min) for 2 h observation. Samples were taken through a sampling port into a 10 mL syringe, filtered using 0.22 μm filters (Millipore, Millex GP) and injected into vials containing sulfide anti-oxidant buffer (Keller-Lehmann *et al.* 2006) or vials/tubes without buffer and analysed for dissolved sulfur species, VFA (Volatile Fatty Acid) and methane. The samples were then stored in a fridge till the entire batch test was completed. Sampling procedures were as described in Mohanakrishnan *et al.* (2008) and Gutierrez *et al.* (2009).

Analytical methods

Filtered liquid samples were collected and analysed immediately for dissolved sulfur species, methane, VFA and soluble and Total Chemical Oxygen Demand (TCOD). Analyses of dissolved sulfur species (SO_4^{2-}, HS^-, $S_2O_3^-$ and SO_3^{2-}) in the liquid phase were measured using ion chromatography (IC, Dionex ICS-2000) using the protocol described in Keller-Lehman *et al.* (2006). VFA concentrations were measured by gas chromatography (PerkinElmer, Inc.). Methane was measured by gas chromatography (Shimadzu GC-9A) using the protocol described in Guisasola *et al.* (2008). Total and soluble COD were determined following the closed reflux colorimetric method 5220D of standard methods (APHA 1998) using a Merck Thermoreaktor model TR 300 and Cary Spectrophotometer Varian 50 Conc UV–visible. Sulfide and methane production rates were calculated from the slopes of the data points using linear regression.

RESULTS AND DISCUSSION

Sulfide and methane production rates in the two systems

Sulfide and methane production rates of the experimental and control reactors measured with batch tests during the three phases described in Table 2 are presented in Figure 2.
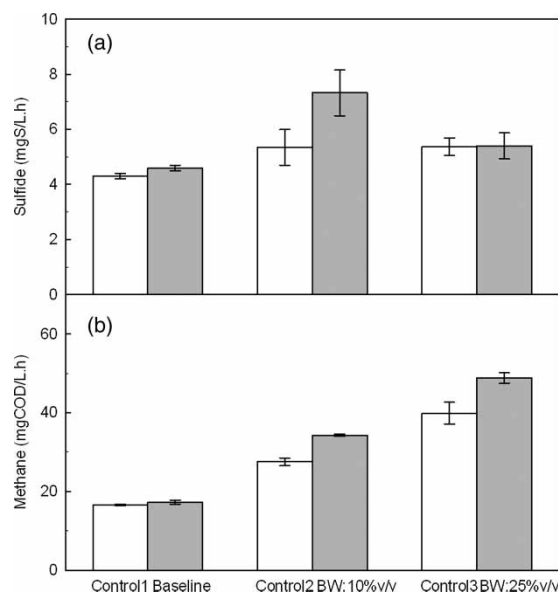
Figure 2 │ Comparison of (a): sulfide and (b): methane production rates with different feed compositions. Note: BW = brewery wastewater.

The *n* value (number of data points used for calculating the error bars) for each phase were 3 data points. By adding 10% v/v of brewery wastewater continuously into the sewer system, the sulfide production rate on average increased by 40% compared to the control reactor. In contrast, by means of 25% v/v brewery wastewater dosing, there was no difference in sulfide generation rates compared to the reference. The discharge of 10% v/v of brewery wastewater to the reactor also increased the methane production rate by 25%. An increment of 22% also occurred when 25% v/v of brewery wastewater was fed into the system. Possible reasons for these varying results will be discussed below.

pH variations and possible inhibitory effects of low pH

Dosing 10% and 25% v/v of brewery wastewater decreased the pH of the sewer system from 7.1 ± 0.1 to 6.6 ± 0.1 and 6.0 ± 0.1, respectively. The pH decreased due to fermentation reactions, as indicated by the increased VFA concentrations. Figure 3 compares the pH and VFA concentrations in the two reactors (control and experimental reactors) during Phase 2 and Phase 3.

A more biodegradable wastewater due to the introduction of brewery wastewater (at both 10 and 25%) enhanced the fermentation process, as evidenced by both the lower pH levels and higher concentrations of VFA. A higher concentration of VFA is expected to increase sulfide production, which was indeed the case with the 10% brewery wastewater addition. However, a further increase of the brewery wastewater fraction to 25% reversed the trend. The sulfide production rate decreased to the level that is similar to that of the control reactor. We hypothesise that the low pH level in this case (around 6.0) substantially inhibited the activity of SRBs as optimal pH has previously been reported to be in the range of pH 7.0–8.0 (Postgate 1979; Visser *et al.* 1996). The inhibition likely compensated for the expected increased rate due to the higher organic load. The results show that the impact of brewery wastewater discharge on sulfide production in sewers is dependent on the amount discharged. A higher discharge of brewery wastewater does not necessarily lead to increased sulfide production.

The addition of brewery wastewater increased methane formation. In both cases, the methane production rate was approximately 30% higher than that in the control reactor. The increase in methane production rate in the control reactor during the experimental course indicated that the reactors did not reach steady state in terms of methanogenesis. However, the use of a control reactor still allowed assessing the impact of brewery wastewater on methane
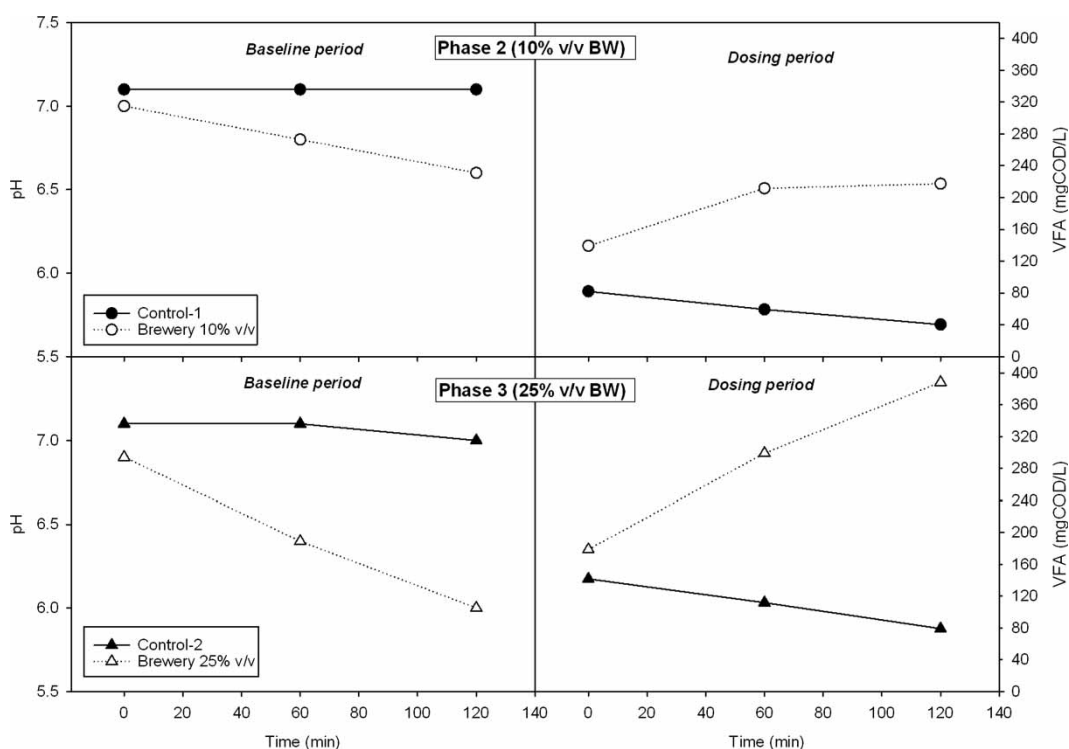

Figure 3 │ Comparison of pH and VFA concentrations in the two reactors during Phase 2 and Phase 3.

production. It is noteworthy that the methane production rate did not increase by a higher percentage in Phase 3 than in Phase 2, despite much higher VFA concentrations in Phase 3. We hypothesise that methanogens were also inhibited by a low pH of 6.0. However, methanogens did not receive the same level of pH inhibition as the SRB. This could be due to the spatial arrangement of the microorganism in sewer biofilms. The thickness of a sewer biofilm can be several hundred micrometres (Mohanakrishnan *et al.* 2008). The competitive advantage of SRB over methanogens could lead to the development of a sulfate-reducing anaerobic zone near the surface of the biofilm, where sulfate is available, and a methanogenic anaerobic zone that lies in a deeper part adjacent to the pipe surface (Guisasola *et al.* 2008). Fermentation likely occurred in the upper layer of the biofilm where fermentable carbon substrates were abundant, resulting in low pH in this zone. The pH in the deeper layers could be higher due to the consumption of VFA by methanogens. However, more detailed studies are required to verify this hypothesis.

Impact of pH on H_2S transfer

pH has a significant impact on the transfer of hydrogen sulfide from wastewater to sewer air in gravity sections of sewers. The 10% and 25% (v/v) addition of brewery wastewater lowered the wastewater pH from 7.1 ± 0.1 to 6.6 ± 0.1 and 6.0 ± 0.1, respectively. The lowered pH could substantially lower the transfer rate of H_2S in the downstream gravity sections.

Rate of hydrogen sulfide transfer from liquid to gas phase in sewers can be calculated as:

$$rH_2S = k_La(H_2S_{aq} - H_2S_{aq}^*)$$

where rH_2S is the rate of H_2S transfer, k_La is the mass transfer coefficient, H_2S_{aq} is the dissolved H_2S in liquid phase, and $H_2S_{aq}^*$ is the equilibrium H_2S_{aq} concentration, which depends upon the gas phase H_2S concentration.

Liquid phase H_2S concentration depends upon the liquid pH and represents a fraction of total dissolved sulfide concentration (H_2S_T), governed by the following equation.

$$[H_2S_{aq}] = \frac{[H_2S_T]}{1 + 10^{(pH-pKa)}}$$

where pKa is the dissociation constant for H_2S_{aq}. At 25 °C, its value is 7.0, which means at a pH of 7.0, 50% of total dissolved sulfide remains as HS^-, while the remaining 50%
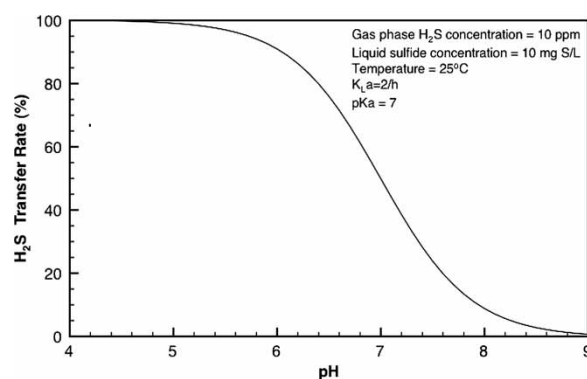
Figure 4 | Impacts of wastewater pH on sulfide transfer rate (H_2S transfer rate at pH = 4 is taken as 100%).

exists as dissolved H_2S gas. The equilibrium concentration of H_2S_g can be calculated using Henry's Law as follows:

$$[H_2S_{aq}^*] = K_{H,H_2S} \cdot p_{H_2S}$$

where K_{H,H_2S} is Henry's constant for H_2S (0.1 mol/L-atm, 25 °C) and p_{H_2S} is partial pressure of H_2S in sewer atmosphere (Hvitved-Jacobsen 2002).

Impact of pH on the hydrogen sulfide transfer rate is illustrated in Figure 4. The key assumptions used in the calculation are shown in the figure.

The results show that the change of pH from 7.0 for normal domestic wastewater to about 6.6 and 6.0 increases the transfer rate from 9.9 to 14.2 and 18.1 mg S/L h respectively for the same total dissolved sulfide concentration of 10 mg S/L. The increases are substantial in both cases. These results suggest that in addition to potentially increasing sulfide production, the discharge of brewery wastewater also substantially increases the transfer rate of hydrogen sulfide from wastewater to sewer air, compounding the odour and corrosion problems.

CONCLUSIONS

The impact on sulfide production of brewery wastewater discharge to sewers is dependent on the amount discharged. The laboratory study revealed a significant increase (40%) in sulfide production rate by discharging 10% v/v of brewery wastewater. On the contrary, no impact was observed on sulfide generation with the discharge of 25% v/v of brewery wastewater. The fermentation of carbohydrates contained in brewery wastewater enhanced the production of volatile fatty acids, which likely enhanced sulfide production. However, the fermentation also lowered pH, which likely had an

inhibitory effect on sulfate reducing bacteria, and is also expected to enhance the transfer of hydrogen sulfide from liquid to gas in gravity sewers. The discharge of brewery wastewater to sewers at both 10% and 25% v/v significantly (30%) enhanced methane production, increasing greenhouse gas emissions from sewers. The future work of the study would be to systematically assess each trade wastewater to determine its specific impact on the biological reactions in sewers.

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REFERENCES

APHA, 1998 *Standard Methods for the Examination of Water and Wastewater*. 20th edition, American Public Health Association. American Water Works Association, Water Pollution Control Federation, Washington, DC.

Baloch, M. I., Akunna, J. C. & Collier, P. J. 2007 The performance of a phase separated granular bed bioreactor treating brewery wastewater. *Bioresource Technol.* **98**, 1849–1855.

Boon, A. G. 1995 Septicity in sewers: causes, consequences and containment. *Water Sci. Technol.* **31** (7), 237–253.

Connaughton, S., Collins, G. & O'Flaherty, V. 2006 Psychrophilic and mesophilic anaerobic digestion of brewery effluent: a comparative study. *Water Res.* **40** (13), 2503–2510.

Driessen, W. & Vereijken, T. 2003 *Recent developments in biological treatment of brewery effluent*. The Institute and Guild of Brewing Convention, Zambia.

Feng, Y., Wang, X., Logan, B. E. & Lee, H. 2008 Brewery wastewater treatment using air-cathode microbial fuel cells. Environmental Biotechnology. *Appl. Microbiol. Biotechnol.* **78**, 873–880.

Fillaudeau, L., Blanpain-Avet, P. & Daufin, G. 2006 Water, wastewater and waste management in brewing industries. *J. Cleaner Prod.* **14**, 463–471.

Foley, J., de Haas, D., Yuan, Z. & Lant, P. 2010 Nitrous oxide generation in full-scale biological nutrient removal wastewater treatment plants. *Water Res.* **44**, 831–844.

Food and Agriculture Organization of the United Nations 2009 Barley malt beer. Agribusiness handbook. European bank for reconstruction and development.

Guisasola, A., de Hass, D., Keller, J. & Yuan, Z. 2008 Methane formation in sewer systems. *Water Res.* **42** (6–7), 1421–1430.

Gutierrez, O., Park, D., Sharma, K. R. & Yuan, Z. 2009 Effects of long-term pH elevation on the sulfate and methanogenic activities of anaerobic sewer. *Water Res.* **43** (9), 2549–2557.

Hvitved-Jacobsen, T. 2002 *Sewer Processes: Microbial and Chemical Process Engineering of Sewer Networks*. CRC PRESS, Washington, DC.

Janhom, T., Wattanachira, S. & Pavasant, P. 2009 Characterization of brewery wastewater with spectrofluorometry analysis. *J. Environ. Manage.* **90**, 1184–1190.

Keller-Lehmann, B., Corrie, S., Ravn, R., Yuan, Z. & Keller, J. 2006 Preservation and simultaneous analysis of relevant soluble sulfur species in sewage samples. In *Second IWA Conference on Sewer Operation and Maintenance, Vienna, Austria, 26–28 October, 2006*. BOKU-SIG, Austria, Vol. 1, pp. 339–346.

Mohanakrishnan, J., Gutierrez, O., Meyer, R. L. & Yuan, Z. 2008 Nitrite effectively inhibits sulfide and methane production in a laboratory scale sewer reactor. *Water Res.* **42** (14), 3961–3971.

Nielsen, P. H. & Hvitved-Jacobsen, T. 1988 Effect of sulfate and organic matter on the hydrogen sulfide formation in biofilms of filled sanitary sewers. *J. Water Pollut. Control Fed.* **60**, 627–634.

Parawira, W., Kudita, I., Nyandoroh, M. G. & Zvauya, R. 2005 A study of industrial anaerobic treatment of opaque beer brewery wastewater in a tropical climate using a full-scale UASB reactor seeded with activated sludge. *Process Biochem.* **40**, 593–599.

Pomeroy, R. 1959 Generation and control of sulfide in filled pipes. *Sewage Ind. Wastes* **31**, 1082–1095.

Postgate, J. R. 1979 *The Sulphate-Reducing Bacteria*. Cambridge University Press, Cambridge, pp. 9–23.

Shao, X., Peng, D., Teng, Z. & Ju, X. 2008 Treatment of brewery wastewater using anaerobic sequencing batch reactor (ASBR). *Bioresource Technol.* **99**, 3182–3186.

Speece, R. E. 1996 *Anaerobic Biotechnology for Industrial Wastewater*. Archae, Nashville, TN.

Spencer, A. U., Nolland, S. S. & Gottlieb, L. J. 2006 Bathtub fire: an extraordinary burn injury. *J. Burn Care Res.* **27** (1), 97–98.

Thistlethwayte, D. K. B. 1972 *The Control of Sulfides in Sewerage Systems*. Butterworths, Sydney.

USEPA 1974 *Process Design Manual for Sulfide Control in Sanitary Sewer Systems*. United States Environmental Protection Agency, Washington, DC.

Visser, A., Hulshoff Pol, L. W. & Lettinga, G. 1996 Competition of methanogenic and sulfidogenic bacteria. *Water Sci. Technol.* **33** (3), 99–110.

Zhang, L., De Schryver, P., De Gusseme, B., De Muynck, W., Boon, N. & Verstraete, W. 2008 Chemical and biological technologies for hydrogen sulfide emission control in sewer systems: a review. *Water Res.* **42** (1–2), 1–12.