

Erratum

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Inhibition of sulfide generation by dosing formaldehyde and its derivates in sewage under anaerobic conditions

L. Zhang, L. Mendoza, M. Marzorati and W. Verstraete

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Decreasing sulfide generation in sewage by dosing formaldehyde and its derivatives under anaerobic conditions

L. Zhang, B. De Gusseme, P. De Schryver, L. Mendoza, M. Marzorati and W. Verstraete

ABSTRACT

Hydrogen sulfide emission in sewers is associated with toxicity, corrosion, odour nuisance and high costs. In this study, a new method to inhibit sulfide generation by means of formaldehyde and its derivatives has been evaluated under anaerobic conditions. The possible impact of formaldehyde on an activated sludge system and an appraisal of the economic aspects are presented as well. A dosage of 19 mg L^{-1} formaldehyde resulted in a decrease of the sulfide production of 90%. Dosing of 32 mg L^{-1} paraformaldehyde and addition of 100 mg L^{-1} urea-formaldehyde were not sufficient to inhibit the sulfide generation in sewage to the same extent. The impacts of 19 mg L^{-1} formaldehyde on activated sludge, in terms of COD removal, nitrification rate and oxygen uptake rates, were negligible. This suggests that formaldehyde dosage is a feasible technique to abate the sulfide problem in sewers.

Key words | biocide, biogenic sulfuric acid, disinfectant, microbial inhibitor, microbially induced concrete corrosion (MICC), sulfate reducing bacteria

L. Zhang
B. De Gusseme
P. De Schryver
L. Mendoza
M. Marzorati
W. Verstraete
Laboratory of Microbial Ecology and Technology (LabMET),
Ghent University, Coupure Links 653,
Ghent B-9000,
Belgium
E-mail: *Bart.DeGusseme@UGent.be*; *Peter.DeSchryver@UGent.be*; *lauramen_2000@yahoo.com*; *Massimo.Marzorati@UGent.be*; *Willy.Verstraete@UGent.be*

L. Zhang
Current address: Department of Resource and Environmental Engineering,
East China University of Science and Technology,
Shanghai 200237,
P. R. China
E-mail: *lezhanghua@hotmail.com*

INTRODUCTION

Hydrogen sulfide (H_2S) production by sulfate reducing bacteria (SRB) in sewer systems and the subsequent emission implies not only odour nuisances and possible health risks, but also severe concrete corrosion by biogenic sulfuric acid (Vincke *et al.* 2002). In Los Angeles, the costs for rehabilitation of the corroded sewers are estimated at €400 million (Sydney *et al.* 1996). In Flanders (Belgium), the economical consequences of sewer corrosion are approximated at €5 million per year (Vincke 2002).

A variety of methods has been developed to cope with the problem such as injection of air or oxygen, dosage of oxidants such as H_2O_2 and NaOCl, precipitation by adding $FeCl_3$ or $FeSO_4$ and dosage of nitrate (Nemati *et al.* 2001; Okabe *et al.* 2003; Garcia De Lomas *et al.* 2005; Nielsen *et al.* 2005). The disadvantages of air and oxygen injection are the limited oxygen transfer (Bowker *et al.* 1992). The effectiveness of chemical oxidants is frequently low because of their reactions with other components in sewage (Bowker *et al.* 1992). In case of oxidation methods and chemical precipitation, operating costs are high (€1.9–7.2 kg^{-1} S removal) (Zhang *et al.* 2008). Dosage of nitrate can be effectively controlled by an upstream H_2S probe in the sewer. However, the operating costs of this technique are often high (€5 per inhabitant per year) (Saracevic & Matsché 2007). Recently, many scientists have given attention to the biological oxidation of sulfide (De Gusseme *et al.* 2008). However, up till now, biological oxidation technologies are neither efficient enough nor cost-effective (€2.1–2.5 kg^{-1} S removal) (Zhang *et al.* 2008). Therefore, new approaches for the control of hydrogen sulfide emission and generation in sewer systems are needed.

It has been reported that the sulfide production by SRB in sewer systems can be decreased by inhibitors such as molybdate and nitrite (Nemati *et al.* 2001). An effective and commonly used biocide is formaldehyde (H_2CO). The commercial product formalin is an aqueous solution (in its typical form 37% formaldehyde by weight, 6–13% methanol and water). The latter liquid disinfectant is widely used in aquaculture to treat ectoparasitic infections (Buchmann & Kristensson 2003). It can be biodegraded by the biological system in wastewater treatment plants (WWTP) (Kajitvichyanukul & Suntronvipart 2006).

In the present study, the inhibition of sulfide generation by dosage of formaldehyde to sewage was examined under simulated sewer conditions. The possible impact of formaldehyde on the subsequent activated sludge system was evaluated by means of COD removal, nitrification rates and oxygen uptake rates (OUR). Additionally, the capability of its derivatives (paraformaldehyde and urea-formaldehyde) to inhibit sulfide generation has been investigated. An appraisal of the economic aspects related to dosing of formaldehyde is presented as well.

MATERIALS AND METHODS

Impact of formaldehyde and its derivatives on sulfide generation

A commercial formaldehyde solution (mass concentration of 36% and density of 1.08 kg L^{-1}) was used to study the impact on sulfide generation. Serum bottles (120 mL) containing different concentrations of formaldehyde (0, 3, 6, 12, 19, 25 and 32 mg L^{-1}) were supplemented with 117 mL sewage and 3 mL inoculum. Two types of inoculum were used. One was the anaerobic sludge taken from a lab-scale upflow anaerobic sludge bed (UASB) reactor in LabMET (Ghent University, Belgium). Another was the anaerobic sediment at 25 g VSS L^{-1} as sampled from a normal city sewer in Ghent (Belgium). The bottles were closed air tight and incubated at 28 °C on a shaker at 100 rpm. The concentrations of sulfide were monitored each day during the course of experiments, using the methylene blue method (Greenberg *et al.* 1992). The indications "S" or "sulfide" describes all species (H_2S, HS^- and S^{2-}). To evaluate the impact on sulfide generation of various concentrations of paraformaldehyde (0, 6, 12, 19, 25 and 32 mg L^{-1}) and urea-formaldehyde (0, 20, 50, 100, 500 and 1,000 mg L^{-1}), similar experiments were performed using sewer sediment as inoculum.

Impact of formaldehyde on activated sludge

The reactors (2 L plastic erlenmeyers) were inoculated with two kinds of activated sludge. One was collected from the Ossemeersen domestic WWTP (Aquafin, Ghent, Belgium). Another was collected from a lab-scale activated sludge reactor in LabMET (Ghent University, Belgium). The reactors contained 1.2 L of mixed liquor (400 mL of activated sludge supplemented with 800 mL of sewage) and were aerated by continuous shaking at 100 rpm at room temperature. Formaldehyde was added to five reactors in different concentrations (6, 12, 19, 25 and 32 mg L^{-1}). A control reactor without formaldehyde was set up as well. After 8 and 20 hours, the reactors were taken from the shaker and allowed to settle for 1 hour. After settling, the supernatant was analyzed for COD and nitrate (expressed as $NO_3^- - NL^{-1}$).

A respirometer consisting of a small reactor vessel (500 mL) was used for the OUR measurements. To measure the dissolved oxygen (DO) concentration, an oxygen electrode was applied, connected to a recorder. Activated sludge (100 mL) and sewage samples (400 mL) containing different concentrations of formaldehyde (0, 6, 12, 19, 32, 76 and 113 mg L^{-1}) were transferred to the vessel and saturated with oxygen by means of aeration with an air pump. When the DO concentration reached 6.0 mg O_2 L^{-1}, aeration was stopped and the DO was measured during the subsequent 20 minutes. The OUR was expressed as mg O_2 g^{-1} VSS h^{-1}. Samples were mixed during the experiment with a magnetic stirrer. The temperature was controlled at 20 ± 0.5 °C.

RESULTS AND DISCUSSION

Impact of formaldehyde and its derivatives on sulfide generation

Dosing of formaldehyde resulted in a decrease of the sulfide production in sewage, both in the case of inoculation with anaerobic sludge as in the case of inoculation with sewer

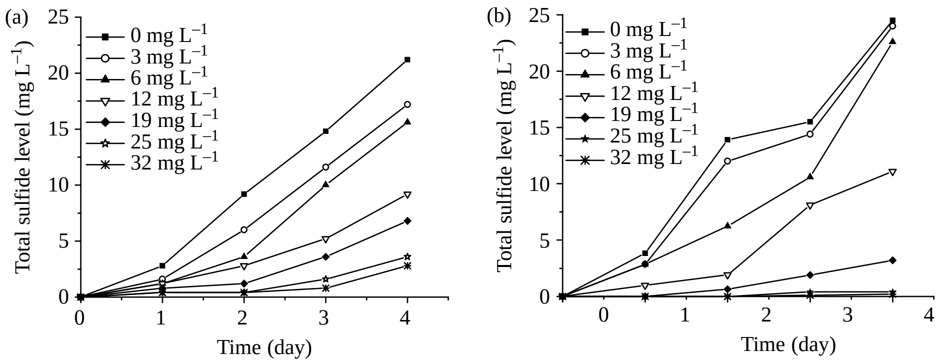

Figure 1 | Sulfide production in sewage supplemented with different concentrations of formaldehyde and inoculated with (a) anaerobic sludge and (b) sewer sediment.

sediment (Figure 1a and b). The more formaldehyde was supplemented to the sewage, the larger the detected decrease. Adding formaldehyde in a concentration higher than 19 mg L^{-1} resulted after 2 days of incubation in a sulfide concentration of less than 1.2 mg S L^{-1} in the sewage with activated sludge (Figure 1a) and a sulfide concentration less than 0.8 mg L^{-1} in the sewage with the sewer sediment (Figure 1b). Addition of formaldehyde to sewage in a concentration of 19 mg L^{-1} was sufficient to obtain a decrease of the sulfide production by SRB of 90% after 2 days. Dosing of formaldehyde in a concentration of 25 mg L^{-1} completely inhibited the sulfide generation in the case of sewage inoculated with sewer sediment.

The effect of paraformaldehyde and urea-formaldehyde on sulfide generation in sewage was not the same extent of formaldehyde (Figures 2 and 3). In the case of paraformaldehyde, a concentration of 19 mg L^{-1} resulted in a decrease of the sulfide generation of about 30% after 2 days of incubation (Figure 2), whereas dosing urea-formaldehyde in the same concentration was only capable of decreasing the sulfide generation by about 20% (Figure 3). Based on this result, it can be stated that formaldehyde is a more effective inhibitor of SRB in sewage then its derivates.

Impact of formaldehyde on activated sludge

To evaluate the possible impact of dosing formaldehyde on an activated sludge system, two reactors with activated sludge were examined. In the reactor, inoculated with Bourgoyen-Ossenmeersen WWTP activated sludge, the COD in the supernatant was 38, 29 and 30 mg L^{-1} after

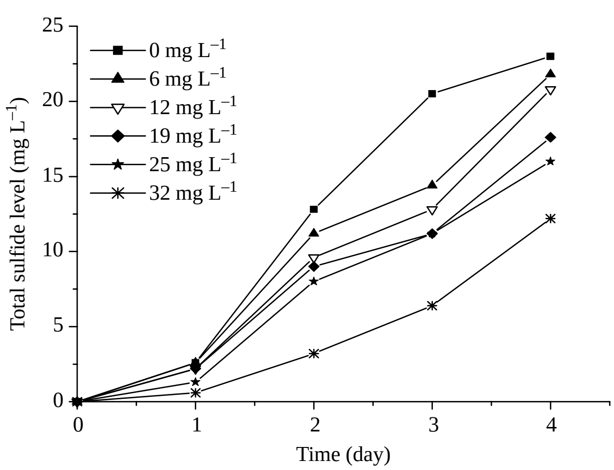

Figure 2 | Sulfide production in sewage supplemented with different concentrations of paraformaldehyde and inoculated with sewer sediment.

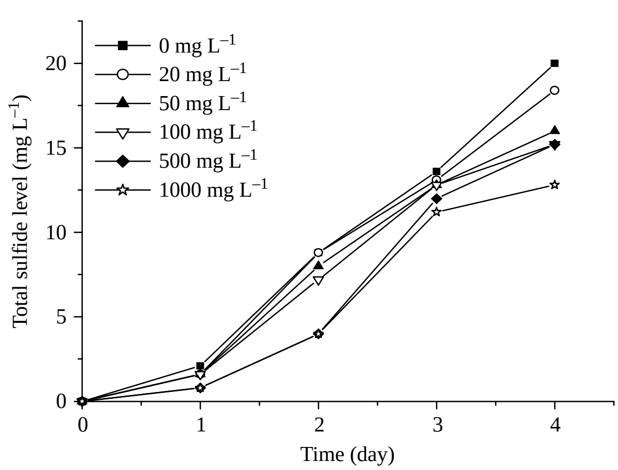

Figure 3 | Sulfide production in sewage supplemented with different concentrations of urea-formaldehyde and inoculated with sewer sediment.

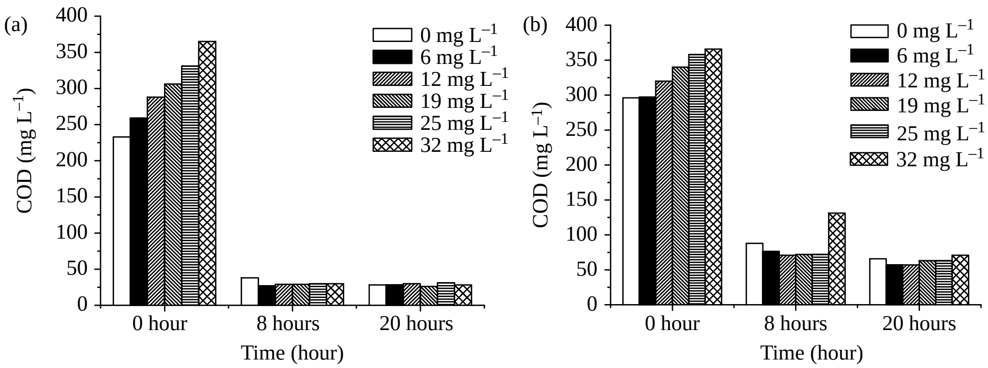

Figure 4 | COD of sewage at different formaldehyde concentrations after inoculation with (a) Ossemeersen WWTP activated sludge and (b) LabMET lab-scale activated sludge.

8 hours at dosages of 0, 19 and 32 mg L^{-1} formaldehyde, respectively (Figure 4a). The nitrate concentrations in the supernatant were 37, 36 and 38 mg $NO_3^- - N\,L^{-1}$ (Table 1). In the reactor, inoculated with LabMET lab-scale activated sludge, the COD in the supernatant was 88, 72 and 131 mg L^{-1} after 8 hours at dosages of 0, 19 and 32 mg L^{-1} formaldehyde, respectively (Figure 4b). The nitrate concentrations in the supernatant were 38, 36 and 26 mg $NO_3^- - N\,L^{-1}$ (Table 1). It is known that formaldehyde can be inhibitory to the nitrification process in aerobic cultures (Eiroa *et al.* 2004). However, our results indicated that the effect on the COD removal and nitrification rate by activated sludge samples was negligible after 8 hours of dosage when the formaldehyde concentration was less than 25 mg L^{-1}.

The OUR was measured as a parameter indicative for the activity of the activated sludge. Without dosage of formaldehyde in the sewage, the OUR for Bourgoyen-Ossenmeersen WWTP activated sludge was 8.86 mg O_2 g^{-1} VSS h^{-1} (Figure 5). All dosages below 32 mg L^{-1} formaldehyde, resulted in an average OUR of 9.30 ± 0.38 mg O_2 g^{-1} VSS h^{-1}. By adding 76 and 113 mg L^{-1} formaldehyde, an OUR of respectively 7.00 and 5.54 mg O_2 g^{-1} VSS h^{-1} could be detected. These results indicated that the OUR remained at a higher level when formaldehyde was dosed at a level below 32 mg L^{-1}. From this findings, it was clear that the impact of adding 19 mg L^{-1} formaldehyde (decrease of sulfide production of 90%) on activated sludge

Table 1 | Effect of formaldehyde on the nitrate concentration (mg NO_3^--N L^{-1}) in the supernatant of reactors inoculated with activated sludge (ND: not detectable).

Formaldehyde (mg L^{-1})	0 h	8 h	20 h
(a) Ossemeersen WWTP activated sludge			
0	ND	37	41
6	ND	37	41
12	ND	38	42
19	ND	36	40
25	ND	39	41
32	ND	38	42
(b) LabMET lab-scale activated sludge			
0	ND	38	46
6	ND	37	53
12	ND	33	46
19	ND	36	46
25	ND	31	45
32	ND	26	44

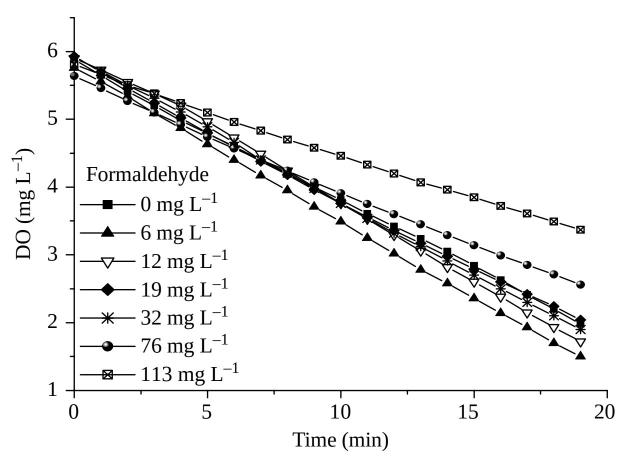

Figure 5 | DO concentrations in the supernatant of a reactor, inoculated with Ossemeersen WWTP activated sludge at different formaldehyde concentrations.

is negligible. As a consequence, this concentration probably has no effect on the receiving activate sludge system. Further research is needed to confirm this hypothesis about the practical implications.

Because of the minor impact of paraformaldehyde and urea-formaldehyde (see above), data of the studies on the impact of the latter compounds to activated sludge systems are not included.

Possible risk to urban environment and health of sewer workers

Formaldehyde is commonly used for the treatment of fish ectoparasites and fungal diseases in aquaculture (Pedersen *et al.* 2007). Discharge of formaldehyde can have a negative impact on the receiving waters. Therefore, its use is strictly regulated (Hohreiter & Rigg 2001). Formalin is generally applied as a single dose treatment. Concentrations frequently used are 25–40 mg L^{-1} formaldehyde as an indefinite treatment or 250 mg L^{-1} formaldehyde for a 1-hour bath (Wooster *et al.* 2005). In this research, dosage of 19 mg L^{-1} formaldehyde was sufficient to decrease sulfide generation in the sewer simulated conditions by 90%. Provided proper operation during dosage, this approach can be rendered applicable for practice. Yet, there is a need to examine in situ how often such single doses are needed. In view of the variable growth conditions in the sewer, a monthly treatment is proposed as a first estimate.

Formaldehyde may be genotoxic or carcinogenic to humans at elevated concentrations (NOHSC 2004). Therefore, precautions are necessary when dosing is considered. The compound is readily soluble in water and reacts substantially and reversibly with water to form methanediol [$CH_2(OH)_2$] (Remzi & Mustafa 2007). The sewer systems are closed, so the exchange between urban atmosphere and the sewer gas phase is limited. However, further study is necessary to investigate the risk to urban environment and health of sewer workers.

Practical implications

Several bacteria can adapt easily to formaldehyde and even use it as an easy degradable organic energy source for heterotrophic growth (Kaszycki *et al.* 2001). Therefore, shock doses should be applied to which adaptation is unlikely. In this way, the bactericidal effect can be maintained in the long term. The possible application of formaldehyde in the proposed dosages should be limited to those spots in the sewer systems with the highest risk to concrete corrosion. Sulfide formation is typically recognized in pressure mains where anaerobic conditions can occur easily due to insufficient reaeration. In gravity sewers located downstream of these mains, high sulfide emission rates can be found, resulting in severe microbially induced concrete corrosion (Yongsiri *et al.* 2003).

Biodegradation of formaldehyde by activated sludge species (e.g. Pseudomonas sp., Rhodococcus sp. and the methylotrophic yeast Hansenula polymorpha) was reported by several authors (Kaszycki *et al.* 2001; Hidalgo *et al.* 2002; Eiroa *et al.* 2004). Kajitvichyanukul & Suntronvipart (2006) reported that formaldehyde can be biodegraded in WWTPs. In this work, at concentrations of 19 mg L^{-1}, there was no negative impact on the activate sludge. In this way, the use of the proposed dosage can offer an environmentally safe method to control the sulfide production in sewer systems.

This work represents a preliminary study on the use of formaldehyde and its derivates in sewage to control sulfide production. Further research is needed to explore the inhibition of sulfide generation by formaldehyde in the sewer environments over a long-term period. In the sewer system, the SRB reside in the biofilm rather than in suspended phase (Widdel 1988). A long-term experiment is necessary to evaluate the adaptation of SRB to formaldehyde and the biodegradation of the biocide in the sewer system and subsequent WWTP.

Economical evaluation

The price of the formalin is €59 per 100 kg (Brenntag NV, Belgium). Provided a sewage production of 250 L per inhabitant per day, approximately 100 m^3 of sewage is supplied to the sewer system per inhabitant per year. When one would apply once a month a shock dose of about 20 mg formalin per L sewage, the chemical cost represent a range of € 0.1 – 0.2 per inhabitant per year. Yet, further research is needed to elucidate how often these doses should be applied in situ. The range in cost calculated on the basis of active sulfide removal avoidance (€1.3–3.6 kg^{-1} S) is located in the same level of biological oxidation technology (€2.1–2.5 kg^{-1} S) and less than other chemical technologies (€1.9–7.2 kg^{-1} S) (Zhang *et al.* 2008). Further research is necessary to explore the actual cost in pilot- or full-scale test.

CONCLUSIONS

The inhibition of sulfide generation by formaldehyde and its derivatives (paraformaldehyde and urea-formaldehyde) has been investigated. Dosing 20 mg L^{-1} formaldehyde is sufficient to obtain a decrease of sulfide generation in sewage of 90%. The impact of formaldehyde on an activated sludge system was evaluated as well. The impact of the latter range of formaldehyde to the COD removal, nitrification rate and OUR was negligible. The economical evaluation demonstrated the opportunities for formaldehyde to be a cost-efficient solution to the problem of sulfide generation in sewer systems.

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