

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

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

### ABSTRACT

Hydrogen sulfide emission in sewers is associated with toxicity, corrosion, odor nuisance and a lot of costs. The possibility to inhibit sulfide generation by formaldehyde and its derivatives (paraformaldehyde and urea formaldehyde) has been evaluated under anaerobic conditions. The impact of formaldehyde on an activated sludge system and an appraisal of the economic aspects are also presented. The optimum dosage to inhibit sulfide generation in sewage was 12–19 mg L<sup>-1</sup> formaldehyde. The dosages of 32 mg L<sup>-1</sup> paraformaldehyde or 100 mg L<sup>-1</sup> urea formaldehyde were not capable of inhibiting sulfide generation in sewage. The impact of 19 mg L<sup>-1</sup> formaldehyde on activated sludge system was negligible in terms of COD removal, nitrification rate and oxygen uptake rate.

**Key words** | activated sludge, concrete corrosion, formaldehyde, sewer, sulfate reducing bacteria

L. Zhang  
L. Mendoza  
M. Marzorati  
W. Verstraete  
Laboratory of Microbial Ecology and  
Technology (LabMET),  
Gent University,  
Coupure Links 653, B-9000 Ghent,  
Belgium  
E-mail: lezhanghua@hotmail.com;  
lauramen\_2000@yahoo.com;  
Massimo.Marzorati@unimi.it;  
Willy.Verstraete@UGent.be

### INTRODUCTION

Hydrogen sulfide emission in the sewer systems is associated with several problems, including toxicity, corrosion and odor nuisance (US EPA 1992). In Los Angeles, the costs for rehabilitation of the sulfide corroded sewers are roughly estimated at €400 million (Sydney *et al.* 1996). In Flanders (Belgium), biogenic sulfuric acid corrosion of sewers costs approximated €5 million per year (Vincke 2002).

Research and development works have produced a number of methods, such as injection of air or oxygen, dosage of H<sub>2</sub>O<sub>2</sub>, NaClO, FeCl<sub>3</sub>, FeSO<sub>4</sub> or 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 (US EPA 1992). The effectiveness of chemical oxidizers is frequently low because of their reactions with other components in sewage (US EPA 1992). Recently, many scientists have given attention to the biological oxidation of sulfide. The cost is high in case of the chemical precipitation and oxidation methods (€1.9–7.2 kg<sup>-1</sup> S) (Zhang *et al.* 2008). Biological oxidation

technologies are not cost-effective (€2.1–2.5 kg<sup>-1</sup> S) or efficient enough (Zhang *et al.* 2008). Therefore, new approaches for hydrogen sulfide emission control in sewer systems are needed.

It has been reported that inhibitors such as molybdate and nitrite can be used to control hydrogen sulfide emission in sewer systems (Nemati *et al.* 2001). Formaldehyde is widely used as an inhibitor to bacteria while 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 under simulated sewer conditions was investigated. The impact of formaldehyde on the subsequent activated sludge system was evaluated by means of COD removals, nitrification rates and oxygen uptake rates (OUR). An appraisal of the economic aspects related to dosage of formaldehyde was also presented. Additionally, the capability to inhibit sulfide generation by its derivatives (paraformaldehyde and urea formaldehyde) has been investigated.

## MATERIALS AND METHODS

### Impact of formaldehyde and its derivatives on sulfide generation

A commercial formaldehyde solution (mass concentration of 36% and density of  $1.08 \text{ kg L}^{-1}$ ) was used to study the inhibition of sulfide generation. Serum bottles (120 mL) containing varying concentrations of formaldehyde (0, 3, 6, 12, 19, 25 and  $32 \text{ mg L}^{-1}$ ) were supplemented with 117 mL sewage and inoculated with 3 mL inocula riching sulfate reducing bacteria (SRB). Two inocula 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 sewer sediment (Ghent, Belgium). The bottles were closed air tight and incubated at  $28^\circ\text{C}$  on a shaker at 100 rpm. The concentrations of sulfide were monitored each day during the course of experiments.

The impact on sulfide generation of the various concentration paraformaldehyde (0, 6, 12, 19, 25 and  $32 \text{ mg L}^{-1}$ ) and urea formaldehyde (0, 20, 50, 100, 500 and  $1,000 \text{ mg L}^{-1}$ ) was evaluated.

### Impact of formaldehyde on activated sludge system

The reactors (2 L plastic erlenmeyers) were inoculated with two kinds of activated sludge. One was the collected from the Bourgoyen-Ossemeersen domestic wastewater treatment plant (Ghent, Belgium). Another was collected from a lab-scale activated sludge reactor in LabMET (Ghent University, Belgium). The reactors containing 1.2 L mixed liquor (400 mL activated sludge mixed with 800 mL sewage) were aerated by continuous shaking at 100 rpm at room temperature. The test consisted of a control reactor without formaldehyde dosage and five reactors with additional formaldehyde dosage (6, 12, 19, 25 and  $32 \text{ mg L}^{-1}$ ). After 8 and 20 hours, the reactors were taken from the shaker and allowed to settle for 1 hour. The settling was followed by a decanting of the supernatant for measurement of COD and nitrate ( $\text{NO}_3^- - \text{N}$ ).

A respirometer consisting of a small reactor vessel (500 mL) was used for the OUR measurements. The vessel contained an oxygen electrode connected to a recorder. Activated sludge (100 mL) and sewage samples (400 mL) containing various concentrations of formaldehyde (0, 4,

12, 38, 76 and  $113 \text{ mg L}^{-1}$ ) were transferred to the vessel and saturated with oxygen by means of bubbling air with an air pump. When the oxygen concentration reached  $6.0 \text{ mg O}_2 \text{ L}^{-1}$ , aeration was stopped and the dissolved oxygen concentration was recorded by the oxygen electrode during the subsequent 20 minutes. Samples were mixed during the test process with a magnetic stirrer. The temperature was controlled at  $20 \pm 0.5^\circ\text{C}$ . The activity measurements resulted in oxygen uptake rates ( $\text{mg O}_2 \text{ g}^{-1} \text{ VSS h}^{-1}$ ) at the various concentrations formaldehyde.

## RESULTS

### Impact of formaldehyde and its derivatives on sulfide generation

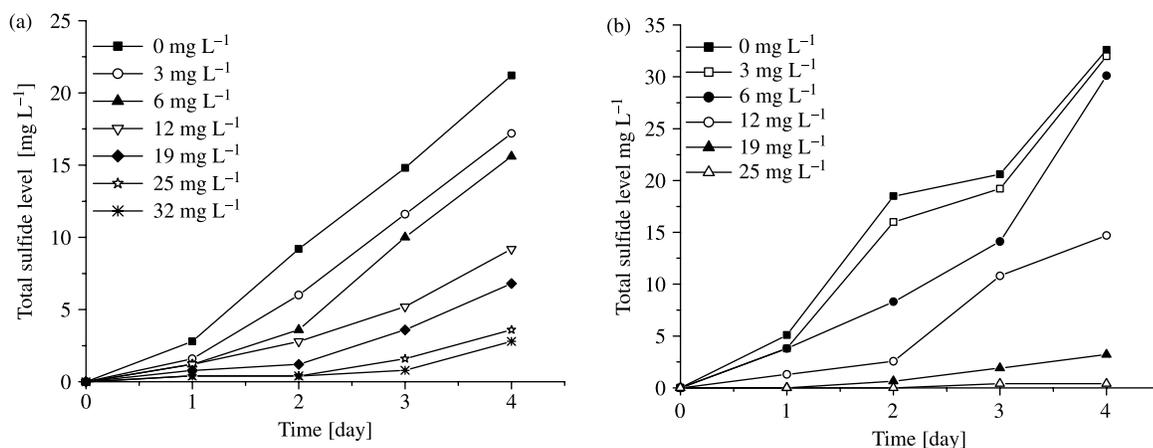
Inoculation with the anaerobic sludge (Figure 1a) resulted in a sulfide concentration of less than  $1.2 \text{ mg L}^{-1}$  after 2 days at a formaldehyde concentration higher than  $19 \text{ mg L}^{-1}$ . Inoculated with the sewer sediment (Figure 1b), the sulfide concentration was less than  $0.8 \text{ mg L}^{-1}$  after 2 days at a formaldehyde concentration higher than  $19 \text{ mg L}^{-1}$ . The total sulfide decreased 90% at a formaldehyde concentration of  $19 \text{ mg L}^{-1}$  for the samples inoculated with anaerobic sludge or sewer sediment, respectively.

The sulfide concentration after 2 days was 12.8, 9.0 and  $8.0 \text{ mg L}^{-1}$  when the paraformaldehyde concentration was 0, 19 and  $25 \text{ mg L}^{-1}$ , respectively (Figure 2). The total sulfide decreased about 30% at paraformaldehyde concentrations of  $19 \text{ mg L}^{-1}$ .

The impact on sulfide generation of urea formaldehyde was neglectable at dosage of urea formaldehyde less than  $100 \text{ mg L}^{-1}$  (Figure 3). After 2 days, the total sulfide decreased about 20% at urea formaldehyde concentrations of  $100 \text{ mg L}^{-1}$ .

### Impact of formaldehyde on the receiving activated sludge system

Inoculated with Bourgoyen-Ossenmeersen activated sludge (Figure 4a and Table 1a), the COD in effluent was 38, 29 and  $30 \text{ mg L}^{-1}$  after 8 hours at dosages of 0, 19



**Figure 1** | Inhibition of sulfide generation by dosage of formaldehyde in sewage inoculated with a) anaerobic sludge and b) sewer sediment.

and  $32 \text{ mg L}^{-1}$  formaldehyde, respectively. The nitrate concentrations in the effluent were  $37$ ,  $36$  and  $38 \text{ mg L}^{-1}$  ( $\text{NO}_3^- - \text{N}$ ). Inoculated with LabMET activated sludge, the COD in effluent was  $88$ ,  $72$  and  $131 \text{ mg L}^{-1}$  at dosages of  $0$ ,  $19$  and  $32 \text{ mg L}^{-1}$  formaldehyde at  $8$  hours, respectively. The nitrate concentrations in effluent were  $38$ ,  $36$  and  $26 \text{ mg L}^{-1}$ . The results indicated that the effect on the COD removal and nitrification rate of formaldehyde was negligible when the formaldehyde was less than  $25 \text{ mg L}^{-1}$ .

Without dosage of formaldehyde in the sewage, the oxygen uptake rate for Bourgoyen-Ossenmeersen activated sludge was  $8.86 \text{ mg O}_2 \text{ g}^{-1} \text{ VSS h}^{-1}$  (Figure 5). When the dosages of formaldehyde were  $4$ ,  $12$ ,  $38$ ,  $76$  and  $113 \text{ mg L}^{-1}$ , their OURs were  $9.54$ ,  $9.50$ ,  $8.85$ ,  $7.00$  and  $5.54 \text{ mg O}_2 \text{ g}^{-1} \text{ VSS h}^{-1}$ , respectively. The results indicated that the OUR

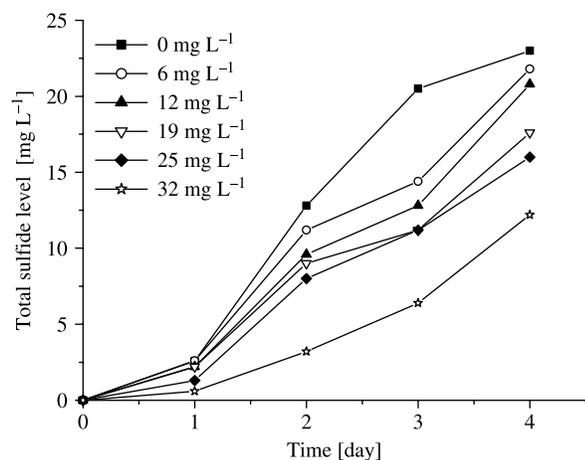
remained at a higher level when formaldehyde was dosed at a level below  $38 \text{ mg L}^{-1}$ .

The dosages of  $32 \text{ mg L}^{-1}$  paraformaldehyde or  $100 \text{ mg L}^{-1}$  urea formaldehyde were not capable of inhibiting the sulfide generation in sewage (Figures 2 and 3). Therefore, the studies of impact of paraformaldehyde and urea formaldehyde on activated sludge systems are not included in this paper.

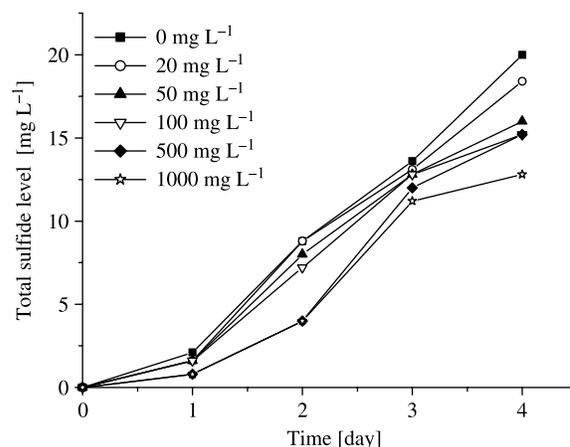
## DISCUSSIONS

### Possible risk to urban environment and health of sewer workers

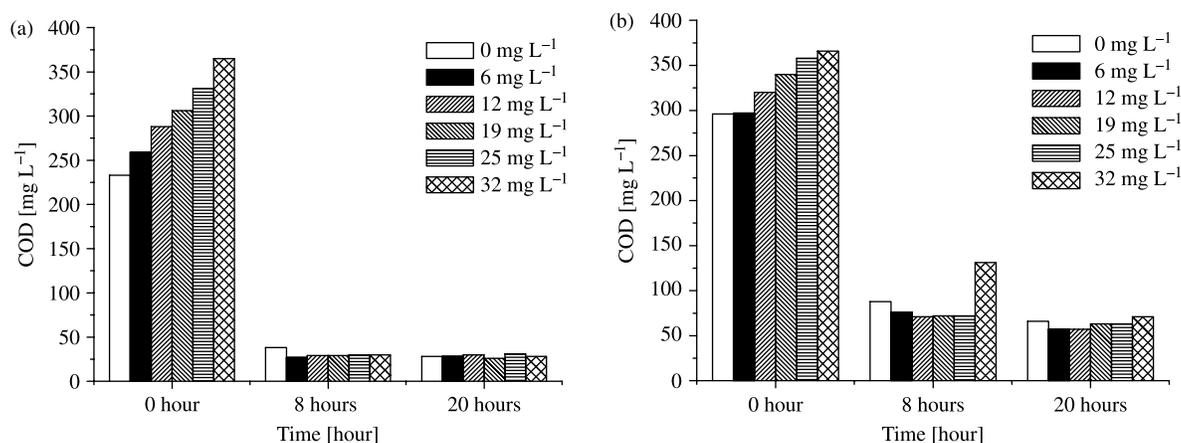
Formaldehyde may be antigenic, toxic or fatal to humans at elevated concentrations (Wooster *et al.* 2005). Therefore,



**Figure 2** | Inhibition of hydrogen sulfide generation by paraformaldehyde in sewage.



**Figure 3** | Inhibition of hydrogen sulfide generation by urea formaldehyde in sewage.



**Figure 4** | COD removal from sewage at different formaldehyde concentration after inoculation with a) Bourgoyen-Ossemeersen activated sludge and b) activated sludge in LabMET.

care is necessary when dosing of formaldehyde is considered. Formaldehyde is commonly used when treating external fish parasites and fungal diseases (Pedersen *et al.* 2007). Concentrations frequently used are 25–40 mg L<sup>-1</sup> formaldehyde as an indefinite bath treatment or 250 mg L<sup>-1</sup> formaldehyde for a 1-hour bath (Wooster *et al.* 2005). In this research, 12–19 mg L<sup>-1</sup> formaldehyde is the optimum dosage to control sulfide generation in sewage. With protection equipment, the operation environment might be acceptable for sewer workers.

**Table 1** | Effect on the nitrate formation (mg NO<sub>3</sub><sup>-</sup>-N L<sup>-1</sup>) of formaldehyde in activated sludge systems

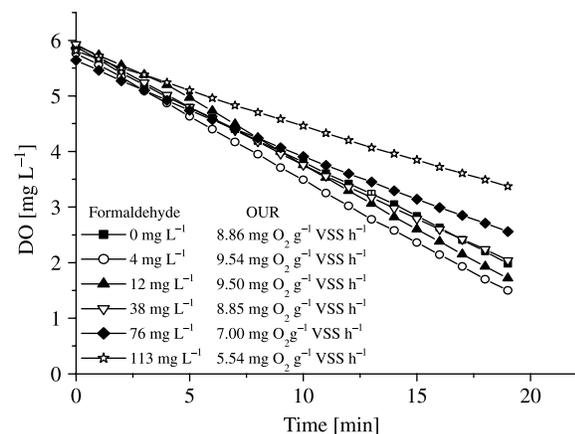
Formaldehyde concentration	0 hour	8 hours	20 hours
a) Bourgoyen-Ossemeersen activated sludge			
0 mg L <sup>-1</sup>	ND	37	41
6 mg L <sup>-1</sup>	ND	37	41
12 mg L <sup>-1</sup>	ND	38	42
19 mg L <sup>-1</sup>	ND	36	40
25 mg L <sup>-1</sup>	ND	39	41
32 mg L <sup>-1</sup>	ND	38	42
b) Activated sludge in LabMET			
0 mg L <sup>-1</sup>	ND	38	46
6 mg L <sup>-1</sup>	ND	37	53
12 mg L <sup>-1</sup>	ND	33	46
19 mg L <sup>-1</sup>	ND	36	46
25 mg L <sup>-1</sup>	ND	31	45
32 mg L <sup>-1</sup>	ND	26	44

ND: not detectable.

Formaldehyde is readily soluble in water and reacts substantially and reversibly with water to form methanediol [CH<sub>2</sub>(OH)<sub>2</sub>] (Seyfioglu & Odabasi 2007). The sewer systems are closed so the exchange between urban atmosphere and gas phase in sewer systems is limited. However, further study is necessary to investigate the risk to urban environment and sewer workers' health of formaldehyde.

### Evaluation of cost

The price of formalin (36–40% formaldehyde) is €59 per 100 kg (Brenntag NV, Belgium). The chemical cost is about €1.6–2.6 per year per inhabitant (250 L sewage per day per inhabitant). The range in cost (€1.3–3.6 kg<sup>-1</sup> S removal) is



**Figure 5** | Oxygen uptake rate test at different formaldehyde concentration OUR: oxygen uptake rate, DO: Dissolved oxygen.

located in the same level of biological oxidation technology ( $\text{€}2.1\text{--}2.5\text{ kg}^{-1}\text{ S}$  removal) and less than other chemical technologies ( $\text{€}1.9\text{--}7.2\text{ kg}^{-1}\text{ S}$  removal) (Zhang *et al.* 2007). Further investigation is necessary to explore the actual cost in pilot- or full-scale test.

### Outlooks

Further investigation is necessary to explore the inhibition of sulfide generation by formaldehyde in the sewer environments over a long-term period test. In the sewer environment, the SRB resides in the sewer biofilm rather than in suspended phase. A long-term test is necessary to evaluate the adaptation of SRB to formaldehyde and the biodegradation of formaldehyde in the sewers.

### CONCLUSIONS

The inhibition of sulfide generation by formaldehyde and its derivatives (paraformaldehyde and urea formaldehyde) has been investigated. The impacts of formaldehyde on COD removal, nitrification rate and OUR were also evaluated. The dosage of  $12\text{--}19\text{ mg L}^{-1}$  formaldehyde was capable to inhibit sulfide generation in sewage. The impacts on COD removal, nitrification rate and OUR of  $19\text{ mg L}^{-1}$  formaldehyde were negligible.

### ACKNOWLEDGEMENTS

This work was supported by project grant G.O.A. 1205073 (2003–2008). The authors thank Peter De Schryver, Yu Zhang and Bart De Gussemé for their critical reading of the manuscript.

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