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Optimization of intermittent, simultaneous dosage of nitrite and hydrochloric acid to control sulfide and methane productions in sewers

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ABSTRACT

Free nitrous acid (FNA) was previously demonstrated to be biocidal to anaerobic sewer biofilms. The intermittent dosing of FNA as a measure for controlling sulfide and methane productions in sewers is investigated. The impact of three key operational parameters namely the dosing concentration, dosing duration and dosing interval on the suppression and subsequent recovery of sulfide and methane production was examined experimentally using lab-scale sewer reactors. FNA as low as 0.26 mg-N/L was able to suppress sulfide production after an exposure of 12 h. In comparison, 0.09 mg-N/L of FNA with 6-h exposure was adequate to restrain methanogenesis effectively. The recovery of sulfide production was well described by an exponential recovery equation. Model-based analysis revealed that 12-h dosage at an FNA concentration of 0.26 mg-N/L every 5 days can reduce the average sulfide production by >80%. Economic analysis showed that intermittent FNA dosage is potentially a cost-effective strategy for sulfide and methane control in sewers.

1. Introduction

The production of hydrogen sulfide in sewers is a well-known problem. Hydrogen sulfide is the primary source of sewer odors (WERF, 2007). Additionally, it can be oxidized into sulfuric acid on concrete surface exposed to sewer air (Hvitved-Jacobsen, 2002). The low pH causes severe concrete corrosion in sewer pipes, manholes and pumping stations. Hydrogen sulfide is also toxic to human and animals (WHO, 2003).

Unlike hydrogen sulfide, it was not until very recently that methane production and emission in sewers became a serious research topic. Several reports found that significant quantities of methane forms in sewers (Foley et al., 2009; Guisasola et al., 2008, 2009). Methane is a persistent and potent greenhouse gas and its emission contributes to the global warming (IPCC, 2006). Uncontrolled release of methane can create possibilities of explosion due to its low explosion limit (approximately 5%) (Spencer et al., 2006). The consumption of

Abbreviations: COD, chemical oxygen demand; FNA, free nitrous acid; HRT, hydraulic retention time; N_2O, nitrous oxide; SRB, sulfate-reducing bacteria; VFA, volatile fatty acid.

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soluble COD by methanogenesis in sewers imposes adverse impacts on the biological nutrient removal processes.

Various chemicals have been used to control hydrogen sulfide production/emission in sewer systems. Among these, oxygen, nitrate, magnesium hydroxide, and iron salts are most commonly used (Pages et al., submitted for publication; Zhang et al., 2008). Oxygen and nitrate can oxidize sulfide chemically and/or biologically (Gutierrez et al., 2008; Mohanakrishnan et al., 2009). Ferric/ferrous salts precipitate with sulfide forming insoluble metal sulfide; and ferric salts also inhibit sulfide and methane production by sewer biofilms (Zhang et al., 2009). $Mg(OH)_2$ elevates wastewater pH, typically to 8.5–9.0, and thus reduces the transfer of hydrogen sulfide from water to the sewer air as well as sulfide and methane productions (Gutierrez et al., 2009). All these chemicals need to be added continuously in order to be effective, thus incurring large chemical consumption and operational costs.

The addition of nitrite for sulfide and methane control in sewers has been tested recently in laboratory sewer reactors (Jiang et al., 2010; Mohanakrishnan et al., 2008). The lab studies showed that the continuous addition of nitrite at 40–120 mg-N/L for three weeks could completely suppress SRB and methanogenic activities. It then took 4–6 weeks for the sulfate reduction capability of sewer biofilms to fully recover. The recovery of methanogenic activity took even longer (50% recovery in 2 months).

It was suggested that nitrite causes specific inhibition on dissimilatory sulfate reduction (Einsiedl, 2009; Greene et al., 2006) and therefore an exposure of sulfate-reducing bacteria (SRB) to a high-level of nitrite caused a gradual decrease of the SRB population and hence the loss of biofilm activity (Jiang et al., 2010; Mohanakrishnan et al., 2008). However, this hypothesis was not supported by the field test results reported in Jiang et al. (2010). The dosage of nitrite at a concentration of 100 mg-N/L for only 33 h over a period of three days achieved the complete suppression of both the sulfate-reducing and methanogenic activities, and the recovery of these activities resembled the re-growth pattern (Jiang et al., 2010). Such effects implied a toxic rather than an inhibitory effect. Jiang et al. (2011) showed that the toxic effect was caused by free nitrous acid (FNA or HNO_2) formed from nitrite rather than by nitrite itself. It was shown that FNA has a strong biocidal effect on anaerobic sewer biofilms. It was found that the viable microbial cells in biofilms decreased from approximately 80% prior to FNA dosage to 5–15% after the biofilm was exposed to FNA at 0.2–0.3 mg-N/L for 6–24 h. The strong biocidal effect of FNA on sewer biofilms implies that the simultaneous dosage of nitrite and acid could achieve rapid inactivation of the SRB and methanogens in sewer biofilms, making it possible to achieve sulfide and methane control through short, intermittent dosages (Jiang et al., 2011).

There are three key operational parameters for an intermittent dosing strategy. They are the concentration of the chemicals (dosing strength), the exposure time (dosing duration), and the dosing interval (repetition frequency). A cost-effective FNA dosing strategy will entail the lowest consumption of chemicals with satisfactory controlling efficiency by optimizing these three parameters.

This study aims to develop a cost-effective dosing strategy for the intermittent, simultaneous addition of nitrite and acid into sewer systems to control sulfide and methane productions. The effects of the above identified parameters, i.e. FNA concentration, exposure time, and dosing intervals, on sulfide and methane productions were investigated experimentally using laboratory-scale sewer reactor systems. Different combinations of these parameters were tested in either single- or multiple-dosage tests in search of the optimal FNA concentration and exposure time. An exponential growth equation was used to describe the recovery of the sulfate-reducing and methanogenic activities following the biofilm exposure to FNA, which supported an economic analysis of the intermittent FNA dosing strategy and its comparison with other sulfide control chemicals.

2. Materials and methods

2.1. Anaerobic sewer biofilm reactors

The laboratory experimental system consisted of four air-tight reactors, namely R1–R4, made of Perspex™ (Fig. 1). Each reactor had a volume of 0.75 L, with a diameter of 80 mm and a height of 149 mm. Plastic carriers (Anox Kaldnes, Norway) of 1 cm diameter were clustered on four stainless-steel rods inside each reactor as biofilm supporters. The total volume of carriers was about 15 mL (2% of the reactor volume). The biofilm area, including both reactor wall and carriers, was 0.05 m^2. The area to volume ratio (A/V) was 70.9 m^2/m^3. The biological activities (i.e. sulfate reduction and methanogenesis) in sewers are primarily occurring in the biofilms (Gutierrez et al., 2009).

Domestic wastewater, collected weekly from a local pumping station, Brisbane (Australia), was used as the feed. The wastewater composition had large variations in sulfate, volatile fatty acids (VFAs), and chemical oxygen demand (COD) concentrations. The sewage typically contained sulfide at concentrations of <3 mg-S/L, sulfate at concentrations between 10 and 25 mg-S/L, and VFA at 50–120 mg-COD/L. Nitrite was below the detection limit. Sulfite and thiosulfate were present in negligible amounts (<1 mg-S/L). The sewage was stored at 4 °C and heated up to 20 °C before being pumped into the reactors.

The reactors were fed with sewage through a peristaltic pump (Masterflex 7520-47) every 6 h, a typical sewage hydraulic retention time in sewers (Hvitved-Jacobsen, 2002). Every feed pumping event lasted for 2 min, delivering one reactor volume (0.75 L) of sewage into each reactor. To ensure homogeneous distribution in reactors, mixing was provided with magnetic stirrers at 200 rpm (Heidolph MR3000).

2.2. FNA dosing schemes

The dosing–recovery experiments were conducted in three consecutive phases, namely the baseline, dosing, and recovery phases. Reactors were operated without FNA dosing to achieve similar sulfide and methane production activities during the baseline phase. During the dosing phase, R2–R4 received nitrite and hydrochloric acid (to achieve the specified FNA concentrations), while R1 was used as the control reactor (no nitrite/acid dosage). Three sets of dosing–recovery tests

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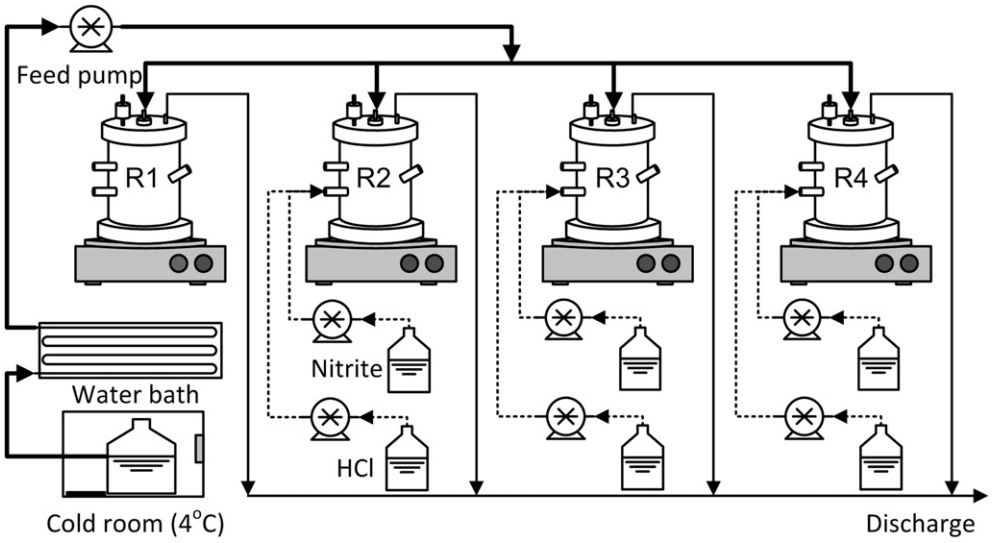

Fig. 1 – The laboratory-scale anaerobic sewer biofilm reactors.

were conducted to investigate the effects of different parameters.

The first set of tests (Tests 1–5) was designed to investigate the effects of FNA concentration and exposure time. The previous study about the biocidal effect of free nitrous acid has indicated that 90% of cell inactivation could be achieved by dosing FNA at 0.26 mg-N/L for 12 and 24 h (Jiang et al., 2011). Thus, the FNA concentrations tested in this study were 0.18, 0.26, and 0.36 mg-N/L (Table 1). The wastewater pH was adjusted to 6–6.2 by adding hydrochloric acid, and was also dosed with 100–230 mg-N/L of nitrite to achieve the selected FNA concentrations (see Table 1). For the FNA concentration of 0.26 mg-N/L, three different exposure times, namely 12, 24, and 96 h, were used in three separate tests to investigate the impact of exposure time on the sewer biofilm activities. For other FNA concentrations (i.e. 0.18, and 0.36 mg-N/L), an exposure time of 24 h was applied. Most of these tests were repeated (Table 1).

The second set of dosing–recovery test was designed to investigate the effects of different dosing intervals (Table 2). Four tests (Tests 6–9) were conducted with multiple dosages, with a fixed FNA concentration at 0.26 mg-N/L, and three dosing intervals, i.e. 4, 8, and 12 days, to investigate the potential impact of dosing intervals on the suppression and recovery of sewer biofilm activities. The exposure times were designed to incorporate those tested in the first stage. An exposure time of 12 h was chosen in most of these tests because it was found to effectively suppress both sulfide and methane productions at the applied FNA concentration. Besides, a multiple-phase dosage of 96 h with a 12-day interval was also trialed to explore the scenarios of excessive exposure.

All the above tests were designed with FNA concentrations and exposure times that were expected to achieve complete suppression of sulfide and methane productions. The third set of tests was designed to explore the possibility of partial sulfide control but potentially complete methane control at low FNA concentrations combined with short exposures. Three dosing–recovery tests (Tests 10–12) were done with an exposure time of 6 h only, at FNA concentration of 0.045, 0.09, and 0.18 mg-N/L (Table 3).

2.3. Batch tests to determine H_2S and CH_4 production

For the dosing–recovery experiments described in Section 2.2, batch tests were conducted prior to, and after the FNA dosing to determine biofilm activities, i.e. sulfate reduction and methanogenesis. The batch tests were performed at intervals from 2 days to 2 weeks. The sulfate-reducing activity was measured under anaerobic conditions as sulfide production rate, and the methanogenic activity was measured as the methane production rate.

Table 1 – The dosing schemes for the single-dosage tests (Test set I) to investigate effects of FNA concentration and exposure time.

Test No.	FNA (mg-N/L)	Exposure (h)	Replications
Test 1	0.18	24	1
Test 2	0.26	12	2
Test 3	0.26	24	2
Test 4	0.26	96	2
Test 5	0.36	24	2

Table 2 – The dosing schemes for the multiple-dosage tests (Test set II) to investigate effects of dosing interval.

Test No.	FNA (mg-N/L)	Exposure (h)	Interval (day)	Dosage
Test 6	0.26	12 → 12 → 12	4	3
Test 7	0.26	12 → 12	4	2
Test 8	0.26	12 → 12	8	2
Test 9	0.26	96 → 96	12	2

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Table 3 – The dosing schemes for the single-dosage tests (Test set III) to investigate the sulfide and methane control at low dosing concentrations and durations.

Test No.	FNA (mg-N/L)	Exposure (h)	Replications
Test 10	0.045	6	1
Test 11	0.09	6	1
Test 12	0.18	6	1

The batch tests were started with pumping fresh sewage into reactors, which lasted for 10 min to ensure a thorough replacement of liquid in reactors with fresh sewage. Wastewater samples were taken at 0, 30, 60, 90, and 120 min after feeding, for the analysis of dissolved inorganic sulfur and nitrogen compounds, as well as methane. Sulfide and methane production rates were calculated using linear regression of sulfide, and methane concentrations, respectively.

2.4. Nitrous oxide measurement by microsensor

Nitrous oxide (N_2O) could be produced when nitrite was added with acid into the anaerobic sewer reactors (Betlach and Tiedje, 1981; Sutka et al., 2006). The monitoring of N_2O production is important because it is a potent greenhouse gas (IPCC, 2006). Wastewater samples were drawn hourly from the reactor, filtered with 0.22 μm membrane into 5 mL capped plastic tubes. Air bubble was completely avoided using parafilm before sealing the tubes. Nitrous oxide microsensor N_2O100 (Unisense A/S, Denmark), with a tip diameter of 70–120 μm, attached to a PA2000 picoammeter (Unisense) was connected to a computer for data logging. It was polarized at a voltage of −0.8 V and calibrated according to the manual. Measurements in the wastewater samples were then carried out with sensor tips dipped into the sample tubes. The sample temperature was also recorded to calculate the dissolved nitrous oxide.

2.5. Acid titration of wastewater

To determine the amount of hydrochloric acid needed to acidify the wastewater to a specified pH, three batches of titration tests were carried out with fresh wastewater ($pH = 7.59 \pm 0.02$). One liter of wastewater in a beaker was gently mixed with a magnetic mixer at 100 rpm, with a pH probe (Metrohm Swiss, 827 pH Lab) placed in the middle to record the pH. Once the pH readings were stable, a small volume (0.1–0.5 mL) of hydrochloric acid (1 M) was added. The new pH value was recorded when getting stable after adding acid. The acid addition and pH recording were repeated till the wastewater pH reached 5.0.

2.6. Chemical analysis

For the analyses of dissolved inorganic sulfur species (sulfide, sulfite, thiosulfate, and sulfate), 1.5 mL wastewater was filtered (0.22 μm membrane) into 0.5 mL preserving solution of sulfide anti-oxidant buffer (SAOB) (Keller-Lehmann et al., 2006). Samples were then analyzed within 24 h on an ion chromatograph (IC) with an UV and conductivity detector (Dionex ICS-2000).

For the analysis of nitrogen species (nitrite and ammonia), 1 mL of sewage was filtered similarly, diluted 10 times and analyzed using a Lachat QuikChem 8000 (Milwaukee) flow-injection analyzer (FIA). FNA concentration is jointly determined by the wastewater pH and the dosed nitrite concentration (Anthonisen et al., 1976; Weon et al., 2002). FNA concentration was calculated as $FNA = (46/14) \times (NO_2^- - N/(K_a \times 10^{pH}))$, where K_a is the ionization constant of the nitrous acid equilibrium equation. The value of K_a is determined by $K_a = e^{-2300/(273+°C)}$.

For methane analysis, 5 mL sewage was filtered (0.22 μm membrane) and injected into vacuumed BD vacutainer tubes using a hypodermic needle attached to a plastic syringe. The tubes were allowed to reach gas–liquid equilibrium overnight. Methane in the gas phase was measured by gas chromatography (Shimadzu GC-9A) equipped with a flame ionization detector (FID). Concentrations of methane in sewage were calculated using mass balance and Henry's law (Guisasola et al., 2008).

3. Results

3.1. Sulfide, methane, nitrite, and nitrous oxide in dosing periods

As an example, Fig. 2 shows the profiles of sulfide, methane, and nitrite during a 24-h dosing period (Test 3). The reactor was replaced with fresh sewage followed by nitrite and hydrochloric acid addition to the pre-designed levels every 6 h. It is clear that no sulfide was accumulating when FNA was present during the whole dosing period. The slight decrease of sulfide (<0.1 mgS/L) during the exposure was likely due to the oxidation by nitrite, either chemically or biologically (Jiang et al., 2010; Okabe et al., 2003a).

In contrast to sulfide, the dissolved CH_4 concentration still increased when FNA was present for the 24-h dosing period. Clearly, methane production persisted although its production was reduced gradually. After the 24 h of FNA dosages, methane production rate was reduced to a negligible

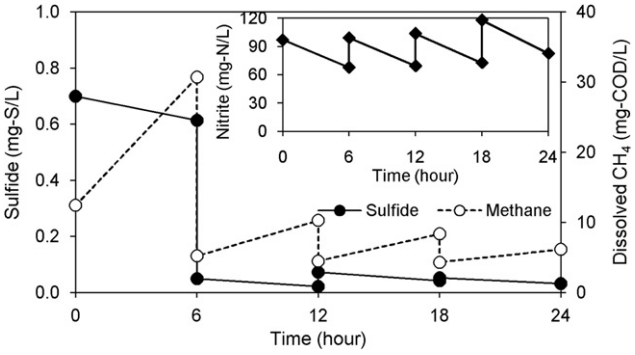

Fig. 2 – Dissolved sulfide, CH_4, and nitrite concentrations in the sewer reactor during a 24 h. FNA dosing period. The reactor was replaced with fresh sewage followed by nitrite and hydrochloric acid addition every 6 h.

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level, i.e. <0.3 mg-COD/L-h. Methanogens, expected to reside in the deep layers of sewer biofilms compared to sulfate-reducing bacteria (Guisasola et al., 2008), were thus likely exposed to a lower level of FNA than the organisms in the outer layers due to the consumption of nitrite (Fig. 2). The biofilm arrangement and structure likely provided a shield against the initial biocidal action of FNA.

The nitrite concentration decreased over all four cycles, suggesting the occurrence of nitrite reduction. However, the reduction rate was about 5 mg-N/L-h in all cycles. Nitrite concentration at the end of each pumping cycle was still above 70 mg-N/L. This implies that a relatively high nitrite concentration can be sustained in the reactor over a long time. While not shown in the figure, pH increased by less than 0.2 in all cycles. As a result of the changes in the nitrite concentration and pH level, the FNA concentration decreased from 0.25 to 0.3 mg-N/L at the beginning of the cycles to 0.1–0.13 at the end of the cycles, which is still strongly biocidal according to Jiang et al. (2010).

The addition of nitrite caused the production of nitrous oxide, which was measured using a microsensor in some of the tests. The highest N_2O was about 1.4 mg-N/L measured at the end of a pumping cycle.

3.2. *Effects of FNA concentration*

Three FNA concentrations, namely 0.18, 0.26, and 0.36 mg-N/L were compared by the dosing–recovery experiments with the same exposure time of 24 h. Fig. 3 shows that sulfide and methane productions reached negligible levels immediately after the FNA dosing event on day 0 (measured in the absence of nitrite and acid). Even at the lowest FNA concentration (i.e. 0.18 mg-N/L), the complete suppression of sulfide and methane productions of sewer biofilm was achieved.

The sulfide and methane-producing activities in reactors gradually resumed after the FNA dosing event. Sulfide production recovered to 50% of the level in control reactor in about 10 days, and then stayed at approximately 70% for the rest of the study. In contrast, methanogenesis recovered much more slowly. At the end of the test (35 days after dosing), it only recovered to 20% even with the lowest FNA dosage.

The results show that the loss and the subsequently recovery of the sulfide- and methane-producing activities of sewer biofilms were similar in all cases. It appears that FNA dosage at 0.18 mg-N/L would be a preferred option among the three due to its effectiveness in suppressing biofilm activities. However, an exposure time of 24 h must be maintained for this FNA dosage.

3.3. *Effects of exposure time*

Three exposure times, i.e. 12, 24, and 96 h, were experimentally compared at the same FNA concentration of 0.26 mg-N/L. Fig. 4 shows that a complete suppression of sulfide and methane productions was achieved with all these exposure times. No significant difference was found between these three cases. The exposure time required by FNA dosage (the simultaneous addition of nitrite and acid) to suppress sulfide production is much shorter than that required by the addition of nitrite alone, which was found to be 2–3 weeks (Jiang et al., 2010).

Both sulfate reduction and methanogenesis started to recover once the FNA dosing event was finished. In two weeks, the sulfate-reducing activity recovered to 70% while methanogenesis reached around 20% only, consistent with the findings reported in Fig. 3. The recovery processes are very similar with all the three different exposure times. Longer exposure time (24 and 96 h) did not further slow down the recovery, in comparison to the 12-h dosage. The exposure time was found to have no prominent impacts on the recovery of sewer biofilm activities.

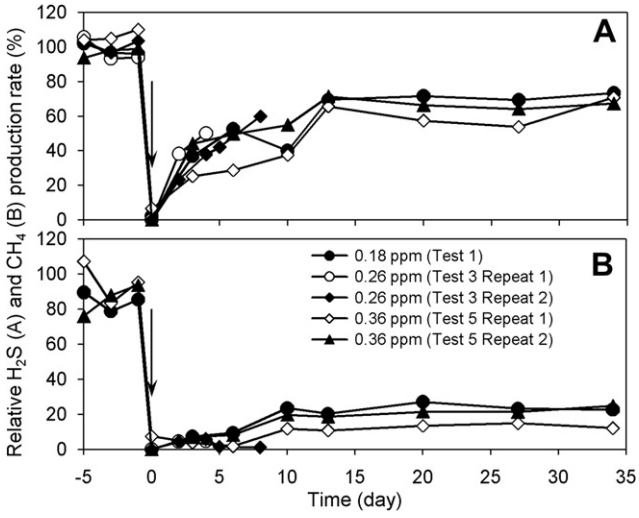

Fig. 3 – The sulfide (A) and methane (B) production rates in the experimental reactors dosed with FNA for 24 h, relative to those of the control reactor (given as %). The vertical arrow indicates the start of the 24 h FNA dosing on day 0.

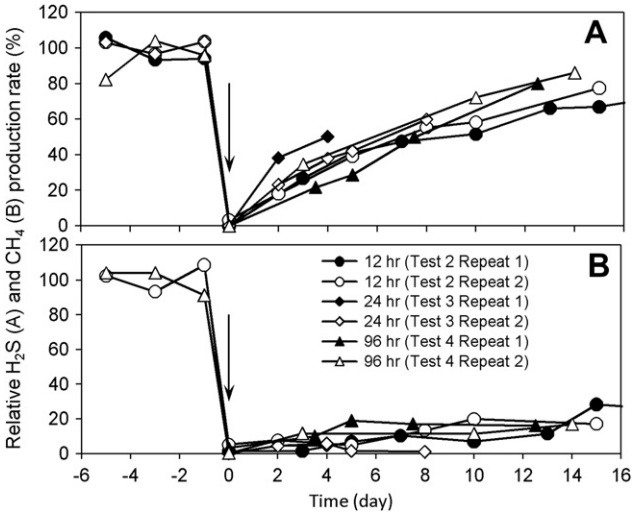

Fig. 4 – The sulfide (A) and methane (B) production rates in the sewer reactors after being exposed to FNA at 0.26 mg-N/L for three different exposure times. The data are presented as percentages of the rates measured on the control reactor. The arrow indicates the start of the FNA dosing on day 0.

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3.4. *Effects of dosing interval*

In addition to FNA concentration and exposure time, dosing interval is another important parameter of an intermittent dosing strategy. Fig. 5 shows the results obtained in Tests 6–9, which were aimed to reveal the potential impact of consecutive dosages with different intervals on the suppression and recovery of the sewer biofilm activities.

It is clear that FNA dosing for a short exposure time of 12 h at an interval of 4 days was very effective in controlling the sulfide and methane production. Sulfide production was reduced by 80% and methane by 90%, averaged over the entire period of the study (Fig. 5A and B). The recovery of the sulfide production activity was similar after all five doses. When the dosing interval was increased to 8 days (at the same dosing level and exposure time, Fig. 5C), the recovery displayed a similar trend to those in Fig. 5A and B. As a result of the extended dosing interval, the average sulfide production rate was reduced by approximately 70%, slightly lower than in the cases of Test 6 and Test 7. Methane production could still be controlled below 10%.

For the extreme scenario with two 96 h dosages at a 12-day interval (Test 9), the sulfide and methane was reduced by 70% and 90%, respectively, averaged over the study period of 33 days (Fig. 5D), similar to the cases of Tests 6–8. However, the chemical consumption was significantly higher (1.5–3 times).

3.5. *Efficacy of low and short dosages*

Test sets I and II employed FNA concentrations and exposure times that were able to suppress sulfide and methane productions completely. Partial control may be achieved with lower FNA concentrations and/or shorter exposure times. Test set III investigated three FNA concentrations, i.e. 0.045, 0.09, and 0.18 mg-N/L. Also, the exposure time was reduced to 6 h.

Fig. 6A shows that the 6-h exposure of sewer reactors to FNA at the above levels decreased the sulfide production rates by 50–80% (varied with the dosing concentration) of that in the control reactor. Complete suppression of methane production was achieved at FNA concentrations of 0.09 and 0.18 mg-N/L, while FNA at 0.045 mg-N/L did not achieve the same level of inhibition. The results again demonstrated that methanogens are more sensitive to FNA than sulfate-reducing bacteria.

After FNA dosing, sulfide production recovered almost linearly for two weeks in all cases, reaching 70–90% of the control level. The recovery rates were similar for the three FNA concentrations. Thus, lower FNA dosage reached higher recovery due to the higher initial sulfide production rate. Eventually, sulfide production recovered to about 80–90% after 30 days. However, it did not fully recover even after 60 days. The recovery of methane production rates was comparably much slower than that of sulfide production rates. After 60 days, methane production for the lowest dosage of 0.045 mg-N/L reached 70% while the other two dosages only recovered to about 40–50%. It is clear that FNA dosage at 0.09 mg-N/L and 6-h exposure time is adequate if methane control in sewers is the primary goal.

4. Discussion

4.1. *Intermittent FNA dosing as a sulfide and methane control strategy*

The impact of three key parameters involved in the intermittent dosage of FNA for sulfide and methane control in sewers, namely the dosing concentration, dosing duration

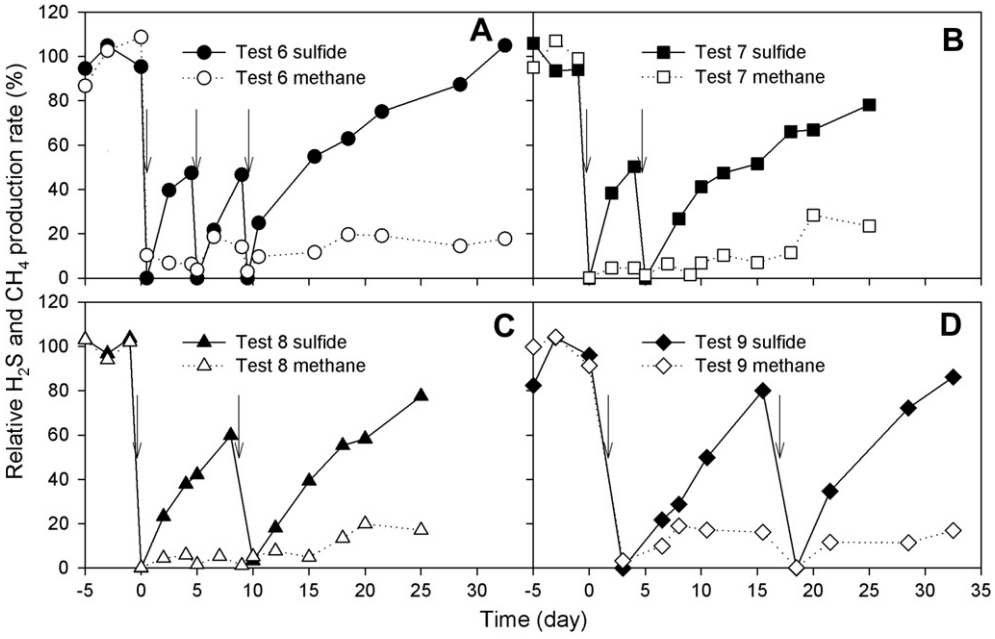

Fig. 5 – The sulfide and methane production rates for multiple dosage experiments. The data are presented as percentages of the rates measured in the control reactor. The arrows indicate the time of the FNA dosing events.

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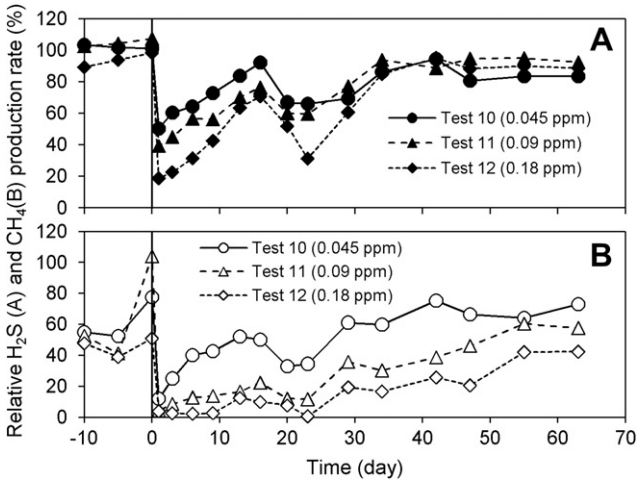

Fig. 6 – The sulfide (A) and methane (B) production rates in sewer reactors before and after being dosed with different concentrations of FNA for 6 h on day 0. The data are presented as percentages of the rates measured in the control reactor.

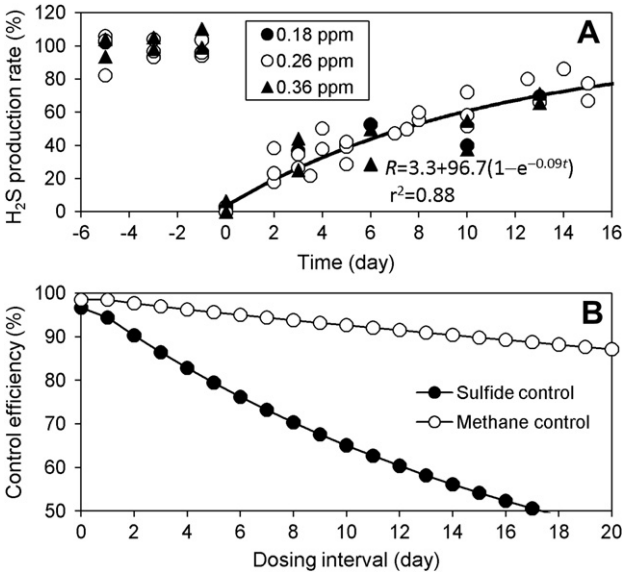

Fig. 7 – (A) The estimation of recovery parameters r_0 and α by dynamic fitting to the recovery data from all the FNA dosage; and (B) the predicted decreases in sulfide and methane control efficiency (%) with time, based on the model obtained in (A).

and dosing interval, was investigated in this study. The experimental data clearly showed that complete suppression of sulfide and methane productions can be achieved when the dosing concentration and dosing duration are above certain levels. While the precise threshold values were not revealed, the experimental results showed that a dosage at an FNA level of 0.18 mg-N/L for a period of 12 h would be adequate for completely suppressing sulfate-reducing bacteria and methanogens in sewer biofilms.

The speed of recovery appeared to be independent of the dosage level or duration as long as complete suppression is achieved during FNA dosage. Also, multiple dosages did not affect the rate of recovery. Because FNA kills biofilm bacteria (Jiang et al., 2011), the recovery of activities reflects the re-growth process of SRB and methanogens. Thus, the recovery rate is mainly determined by the doubling time of sulfate-reducing bacteria and methanogens.

The recovery data of sulfide production obtained in all single-dosage experiments are well described by an exponential recovery equation $r = r_0 + (100 - r_0)(1 - e^{-\alpha t})$ ($R^2 = 0.88$, Fig. 7A), where $r_0 = 3.3\%$ is the residual sulfide production rate immediately after FNA dosing, $\alpha = 0.09\ d^{-1}$ is the recovery constant. The exponential rising pattern of the recovery resembles the bacterial re-growth. This implies that SRB and methanogens redeveloped in the sewer biofilm after stopping the dosage.

The above model supports the design of the dosing frequency required for achieving certain levels of sulfide (and methane) control. The dependency of control efficiency on the dosing interval calculated using the above model is shown in Fig. 7B. For example, a dosing interval of approximately 4 days is required to maintain a sulfide control efficiency at >80%. In contrast, less frequent dosage of FNA (one dose every 20 days) would be needed for methane control.

4.2. *Economic analysis and comparison with other strategies*

The FNA dosing involves the addition of two chemicals, nitrite and acid, to sewers simultaneously. The FNA concentration is highly sensitive to the wastewater pH. The amount of nitrite required to make up a certain FNA concentration can be reduced by 10 times when pH is decreased by one unit. Fig. S2 compares the nitrite and acid costs (prices/costs are given in US dollars) as a function of pH. The chemical costs for nitrite decrease dramatically from \$0.85/m^3 at pH 7.5 to \$0.03/m^3 at pH 6, to achieve an FNA concentration of 0.26 mg-N/L. Such a saving in nitrite is achieved with only a slight increase (\$0.01/m^3) in the acid costs. The acid consumption to adjust the pH was calculated from the wastewater titration results shown in Fig. S1. Thus, a lower pH is preferred from an economic point of view. However, a too low pH can cause potential corrosion of sewer pipe and installations. A pH level of 6.0 appears to be an appropriate choice as it is not harmful for sewer concrete (communication with industry partners).

The experimental results show that an FNA concentration of above 0.18 mg-N/L is adequately biocidal for sewer biofilm activities. To be on the conservative side, we use 0.26 mg-N/L in the economic analysis. The experimental and modeling results show that an exposure time of 12 h and a dosing interval of 4.5 days would be adequate for achieving an overall sulfide control efficiency of 80%. In the analysis, it was assumed that the average sulfide concentration was 15 mg-S/L in the absence of a control measure. Table 4 compares chemical costs of intermittent FNA dosing with other chemicals reported in literature.

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Table 4 – Comparison of chemical addition costs to control sulfide in sewers.

Chemicals	Control efficiency (%)	Cost ($/m^3)	Cost ($/kg-S)	References
FNA[a]	>80	0.03	2.2	This study
$Ca(NO3)_2$ [b]	100	0.07–0.12	11–19	Bertrán de Lis et al. (2007)
$Fe(NO_3)_3$ [b]	100	0.6	24	Bertrán de Lis et al. (2007)
$FeCl_2$ [b]	100	0.1	11.5	Bertrán de Lis et al. (2007)
$FeCl_3$ [b]	100	0.07	8	Saracevic et al. (2006)
$NaNO_3$ [c]	100	–	16.5	Jenneman et al. (1986)
$NaNO_3$ [c]	65	–	0.6	Okabe et al. (2003a)
$NaNO_3$ [c]	100	–	3.4	Okabe et al. (2003b)
$NaNO_3$ [c]	90–95	–	3.4–11.2	Yang et al. (2005)
$Ca(NO3)_2$ [c]	100	–	5.9	Rodriguez-Gomez et al. (2005)
$FeCl_2 \cdot 4H_2O$ [c]	90	–	30.2–35.2	US EPA (1992)
$FeSO_4 \cdot 7H_2O$ [c]	95–97	–	6.5	Tomar and Abdullah (1994)
$FeCl_3$ [c]	100	–	5.0	Nielsen et al. (2005)
H_2O_2 [c]	90–95	–	5.4–5.7	US EPA (1991)
H_2O_2 [c]	87–100	–	4.7	Tomar and Abdullah (1994)
Pure O_2	80–90	0.04	4.8–10.8	MMBW (1989)
Air	90	0.11	–	Saracevic et al. (2006)

a Assuming average sulfide concentration of 15 mg-S/L in sewers. Costs are estimated based on chemical prices in US $: $150.00/ton for 32% hydrochloric acid, and $550.00/ton for $NaNO_2$, http://www.alibaba.com.
b Estimated data from the respective references.
c Excerpt from Zhang et al. (2008).

The estimated cost of FNA dosing to achieve 80% control is $0.03/m^3 or $2.10/kg-S. The chemical cost of nitrate, ferric/ferrous and H_2O_2 dosing was much higher than FNA (Table 4). It is clear that the intermittent FNA dosing is more cost-effective compared to the addition of other widely used chemicals. The intermittent dosing strategy greatly reduces the chemical consumption in comparison to the continuous addition of chemicals, such as iron, oxygen, nitrate, and $Mg(OH)_2$. Further investigation is required to obtain the actual cost (based on local chemical prices) in real sewers.

The additional advantage of FNA dosage is the suppression of methane production. This will subsequently reserve more soluble COD for the nutrient removal in downstream wastewater treatment plants, supported by higher VFA in effluent from reactors dosed with FNA (Fig. S3). While oxygen and nitrate addition are also expected to suppress methane formation, both oxidize organic carbon to CO_2.

One adverse aspect of FNA dosing is the production of N_2O. The average N_2O production rate measured during dosing periods was 0.23 mg-N/L-h. N_2O is an electron acceptor for denitrifiers, and therefore its further reduction to N_2 by denitrifiers is expected when nitrite is consumed to low levels in downstream sections. When N_2O containing wastewater is discharged to gravity sewer, N_2O stripping to the sewer gas phase will likely occur particularly under turbulent conditions. Precautions should be taken in planning FNA dosage, including timing and location, to prevent the unwanted N_2O release.

A further potential problem is that the lower pH during dosing period can enhance the H_2S transfer from liquid to the sewer gas phase. However, there will be negligible H_2S in the liquid when FNA is present. In real application, FNA should be added section by section in a sewer network rather than at all places simultaneously. Nitrite will thus be diluted before arriving at the wastewater treatment plants. This can avoid the adverse shock to biological treatment processes by high nitrite concentrations.

5. Conclusions

This study investigated the intermittent dosing of free nitrous acid to control sulfide and methane production through dose-recovery experiments in sewer reactors. The three key parameters, i.e. FNA concentration, exposure time, and dosing interval, of the intermittent dosing strategy were optimized by single and multiple-dosage tests. The main conclusions are as follows.

- FNA concentration at 0.26 mg-N/L or above, with an exposure time of 12 h or longer, could suppress sulfide and methane production by sewer biofilms. However, the sulfide and methane production rates recover gradually following the FNA dosage, with a pattern resembling that of bacterial re-growth. To reduce sulfide production by 80%, a dosing interval of 4.5 days is required.
- When methane control is the primary goal, lower FNA dosage (e.g. 0.09 mg-N/L) and shorter exposure time (e.g. 6 h) can completely suppress methane production. Also, a long dosing interval (e.g. 20 days) would be adequate to achieve 90% control efficiency.
- The intermittent FNA dosing strategy developed in this study is more cost-effective than other chemicals commonly used by water industry. However, field tests are required to verify the effectiveness and benefits of the proposed dosing strategy.

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Appendix A. Supplementary information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.watres.2011.09.009.

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