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Laboratory test method of chemicals to reduce emissions of H_2S and odours in wastewater

Wolfram Franke[1#], Tom Granli[1], Guido Kuhn[2] and Rune Bakke[3]
[#] Corresponding author
[1] Yara Technology Center, Hydrovegen 67, 3908 Porsgrunn, Norway.
Wolfram.Franke@yara.com and Tom.Granli@yara.com
[2] Yara Industrial GmbH, Sprudelstraße 3, 53557 Bad Hönningen, Germany.
Guido.Kuhn@yara.com
[3] Institute for Process-, Energy- and Environmental Technology at Telemark University College (TUC), Postbox 203, 3901 Porsgrunn, Norway. rune.bakke@hit.no

Waste water systems tend to be a source of odours as a result of transporting odorous substances as well as sewers being large biochemical reactors. Waste water in pressure mains and long non-turbulent gravity sewers turns anaerobic if not conditioned. The result is hydrogen sulphide (H_2S) and odorous volatile organic compounds (VOCs) emissions. These emissions must be controlled and limited to comply with environmental legislation as well as safety demands.
A common method to reduce the emissions is dosing chemicals into the wastewater resulting in changed conditions, altered microbial activity and stimulation of oxidizing reactions.
Chemicals for this purpose have to be tested and approved before use in order to make sure that technical effects, ecological compatibility and costs (customer & producer) are beneficial. For such investigations we have developed a three step investigation procedure: 1. Testing chemicals in simultaneously run batch tests. 2. Testing chemicals in a continuously fed loop reactor. 3. Field testing in a large scale sewer under well known conditions. Synthetic wastewater is used for the first and second steps. Step 1 of the investigation is the focus of this paper.
The developed method uses 250 ml reactors with biofilm carriers and constant stirring. Waste water is changed periodically. The main target of the method is the comparison of different chemicals and dosages of these. Several parameters are investigated including headspace H_2S analysis. Experimental results demonstrate that the method clearly distinguishes effects of different agents and dosages of these.

1. Introduction

Waste water is a source of odorous emissions, both because of the materials it contain and the chemical and biological processes that take place. Sewers can be regarded as being large biochemical reactors. Microbes in biofilms in contact with waste water degrade organic matter. In untreated pressure mains and long non-turbulent gravity

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sewers the water tends to turns anaerobic. The result in most cases is the emission of H_2S and VOCs. These emissions must be controlled and reduced to comply with environmental legislation and safety regulations. Odor is an issue that is still only limited within individual state laws and guidelines. H_2S however has become more in focus and is limited by 2009/161/EU (EU, 2009) referring to 98/24/EC (EC, 1998) because of its hazardous character. Thus prevention of H_2S emissions is of increasing importance for operators within the EU.

A common method to reduce the emissions from sewer systems is dosing chemicals into the wastewater. This conditioning alters the microbial activity and/or stimulates oxidizing reactions, depending on which chemicals are used: like Nitrates to prevent septicity, Iron salts to bind sulphide produced under septic conditions or the use of heavy oxidizers alone or in combination. Details on the task and state of the art dosing strategies can be found for example in FRECHEN et al. (2008), FREY (2009), LUCAS et al. (2009), guideline ATV DVWK M-154 or patent WO/2007/046705 A1.

Chemicals for this purpose have to be tested and approved before use. Technical effects and ecological compatibility have to be demonstrated, and the costs associated with the treatment must be acceptable to the user.

We have established a three steps investigation procedure to check the technical effects of new agents:

1. Run batch test on multiple samples simultaneously, using 250 ml reactors with biofilm carriers and electrochemical H_2S gas monitors together with classic chemical analysis.
2. Run continuously fed reactor simulating sewer conditions for increased degree of reality, using chemical analysis for monitoring.
3. Field testing in large scale sewers under well defined conditions.

The aim of this paper is to describe and evaluate the first of the three steps; the batch test procedure.

2. Methods and Materials

2.1 Reactor system and waste water

There are several possibilities to create a test system. In the following some issues of importance are discussed leading to the establishment of an investigation procedure in three steps. Advantages and disadvantages for the different systems are summarized in Table 1.

The batch test in small reactors is chosen for screening tests as many reactors can easily be run simultaneously. In this setup biofilms move on plastic carriers in the liquid phase. Unfortunately, biofilm micro organisms are exposed to aerobic, anoxic and septic conditions in this test, which is not always the case in sewers. For an initial screening the batch test still provides best relation between effort and outcome.

Table 1: Comparison of different test methods

System	Pros	Contras
Batch test ("bottle test") with synthetic wastewater and refill on a regularly basis	- Easy to handle Bio film activity detectable	- No plug flow Bio film changes between aerobic, anoxic and septic conditions
Loop with permanent feed of synthetic waste water and circulation	- Bio film activity detectable - Continuous system - high shear forces induced by recirculation	- Maintenance - no plug flow - bio film-diameter-relationship unrealistic
Sewer (parallel-minisewer-system, driven with waste water)	Comparison of different dosages for the same waste water possible	- Expensive - Maintenance
Sewer (large scale)	Realistic conditions	only one treatment can be tested at the time Lack of control with changing conditions

The batch reactors were made of 250 ml bottles (Schott) filled with liquid (synthetic waste water) and carrier material (in this case KMB carriers (need to do a search in literature to find a proper reference?)). The synthetic waste water was changed daily, so it is a batch test with regular replacement, which can be defined as a fed batch process. The synthetic waste water was mixed according to EC 648/2004 (EC 2004), but higher feed organics concentration than this standard was used in order to have no food limitation. The concentrations of all compounds of the synthetic waste water were doubled to increase the reactivity and decrease the total experimental time. A total amount of 21,5 g or 125 pieces of clean KMB biofilm carriers were used in each bottle (delivering approximately 550 cm^2 biofilm area).

2.2 Measurements

The following parameters were measured:

- Septicity [Resazurin: colour indicator for change from anoxic to septic conditions]
- Redox potential (ORP) [VWR ORP 15]
- Hydrogen sulphide (H_2S) [Apptek OdaLog 0...200 H2S and 0...1000 H2S]
- Sulphide [Merck Microquant (MiQ) Sulphide. Res.: 0.1, 0.3, 0.5, 0.7, 1, 2, 3, 4, 5]
- Nitrate (NO_3^-) [Merck RQflex 10; Merck Reflectoquant 5…225 mg/L NO_3^-]

All measurements were made in liquid samples with the exception of H_2S which was measured in headspace. At the time of developing the "bottle test" method only standard bottles were available. Hence a simultaneous investigation of undisturbed headspace and liquid phase was not possible. In order to improve this method, bottles with two access connectors for sampling were used.

Figure 1: Bottle test with an H_2S measurement device attached to the reactor

3. Results and discussion

3.1 General comment

In the following some results are presented For evaluation purposes. As substances tested are not the focus of this paper, they are denoted "Agent A" and "Agent B".

3.2 Liquid analysis

The method was verified by confirming that the nitrate removal activity was in the biofilm and not in the bulk phase. This was done indirectly by monitoring nitrate consumption in a bottle with biofilm on carriers compared with consumption in a bottle without biofilm but where 10 ml of microbially active liquid remained from previous run as inoculum. The graphs in Figure 2 Left) show that in a reactor with carrier material NO_3^- is consumed while the concentration of NO_3^- stays stable without the biofilm carrier material.

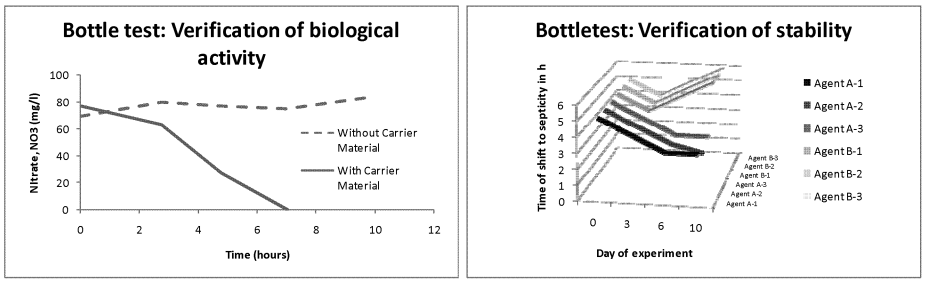

Figure 2: Left) Verification of biological activity being primarily (solely) in the biofilm by monitoring Nitrate consumption with and without biofilm. Right) Verification of reproducibility by monitoring incubation time before occurrence of septicity.

Test results were reproducible and independent from reactors, as seen in tests with the same dosage in different reactors in parallel (Figure 2 Right)). The diagram shows the

development of the point of time (as hours after refilling) when the liquid in the reactors changes into septic conditions (Resazurin turns colourless). In this case it can be seen, that Agent B performs better than Agent A (as a consequence of increased microbial activity), as the occurrence of septicity is delayed more and more for agent B while it comes sooner for A .

The results from another test with several runs using different Agent A dosages are presented in Figure 3. The trend of this dose-response-test is obvious: The higher the dosage of Agent A is, the lower is the sulphide concentrations, implying lower sulphide production rates.

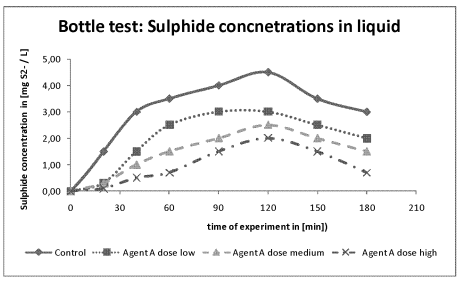

Figure 3: Results from a dose response test

3.3 Headspace analysis

The headspace H_2S analysis, which demands tight sealing and proper sensors, is presented in Figure 4. The tightness of three different seals tested using the same bottle, the same measurement device and the same initial headspace gas composition is demonstrated in figure 4 Left). The development of H_2S in headspace in the three runs is similar implying that all tree methods are adequate. However, the decrease of H_2S itself indicates a challenge for the measurement: H_2S is measured electrochemically and thereby consumed. Half of the headspace H_2S is consumed in two hours, showing that this consumption is significant. A model to compensate for the sensor's consumption is required for interpretation of test results. However, for short term H_2S measurements, the used Odalogs seem to be acceptable.

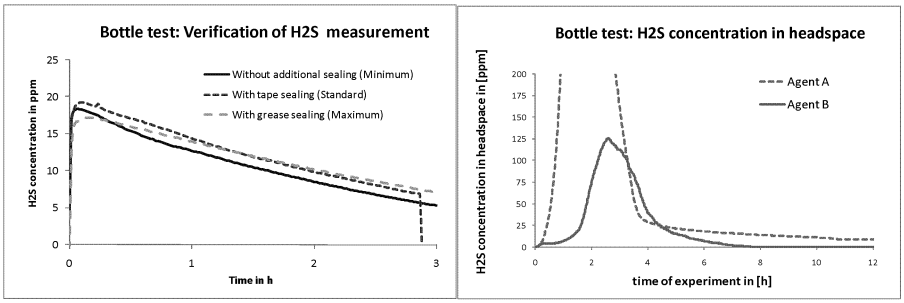

Figure 4: Left) Verification of H2S headspace test – especially focussing on the sealing; Right) Results of a comparison of two different agents

Figure 4 Right) shows results from a comparison test. There Agent B suppresses H_2S production longer and to a much greater extent than Agent A. Obviously the method is able to separate effects of different agents and dosages, and is therefore suitable for screening tests.

4. Conclusion

Odorous emissions from sewers must be controlled and limited. This can be done by dosing chemicals into the wastewater resulting in changed conditions, alteration of the microbial activity and/or stimulation of oxidizing reactions. A systematic three steps investigation to check effects of agents for odour control in sewers is presented. A fed batch test on multiple samples run simultaneously is found to be the most efficient first step to screen agents and dosages. The batch reactors are glass bottles filled with plastic media for biofilm growth, where feeding is done by replacing the liquid phase on a regular (daily) basis. Experimental results demonstrate that the method clearly distinguishes effects of different agents and dosages of these.

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