

Use of microaerobic conditions for the improvement of anaerobic digestion of solid wastes

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ABSTRACT

The treatment of solid wastes containing slowly biodegradable compounds or high level of sulphur compounds was carried out. In both cases the application of microaerobic conditions (that means controlled dosing of small amount of air or oxygen into digester) was an efficient tool to increase the biodegradability of treated material and/or to increase the activity of methanogenic bacteria by removal of their inhibitor.

Key words | anaerobic digestion, biodegradability, biomass activity, microaerobic, oxidation-reduction potential, sulphide oxidation

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INTRODUCTION

Anaerobic digestion is a common process for the treatment of solid wastes, which enables energy recovery from biomass and waste materials. Very often the biodegradability of such wastes is limited due to the nature of organic material, an inhibition of anaerobic bacteria or for other reasons. Several recent studies have showed that a limited presence of the oxygen in the digester is not dangerous, even can be positive in some aspects. (Khanal & Huang 2003a; Tang *et al.* 2004; Jenicek *et al.* 2005; Krishnakumar *et al.* 2005; van der Zee *et al.* 2007)

The strict border between anaerobic and aerobic processes has become fuzzier during the last years. Different combinations and interactions of both processes have been studied and microaerobic experiments where one of the major topics (Noparatnaraporn *et al.* 1986; Zacharias *et al.* 1995; Eriksen *et al.* 2008). Microaerobic conditions are obtained by dosing of a limited amount of air (oxygen) into anaerobic reactor. It was shown that anaerobic bacteria including methanogens can be active also in such system. In a mixed culture, even strict anaerobes can survive without any inhibition, if facultative microorganisms are able to consume the present oxygen quickly and fully.

The definition of the microaerobic conditions is not fixed yet. However, the microaerobic system can be

characterized as a system with zero concentration of oxygen and limited (trace) consumption of oxygen. The oxidation-reduction potential (ORP) can be used for the control of microaerobic systems. While in fully anaerobic system the ORP varies between -200 and -300 mV (related to silver chloride electrode), by dosing of oxygen the ORP is increased of about $30-50$ mV (Khanal & Huang 2003b; Pitter *et al.* 2005). Therefore, the microaerobic system can be defined generally as the system in which micro-consumption of oxygen causes a limited ORP increase.

Until now, the microaerobic conditions were predominantly used for hydrogen sulphide removal from biogas (Buisman *et al.* 1990; Janssen *et al.* 1999; Khanal & Huang 2003a). The microaerobic technological methods in use differ in the technique of the air dosing. The first one is introducing the air into the gas space of the digester. The advantage of this method is a lower required flow rate of air. On the other hand, problems with precipitation of the elemental sulphur in gas pipes and other improper places may occur sometimes. The second method introduces the air into the recirculation stream of the digester. In such case, a bigger amount of air is required, as a certain part of oxygen can be consumed by other processes in addition to H_2S oxidation (van der Zee *et al.* 2007).

In the presented study the second method was applied. The influence of the surplus oxygen has to be studied, because of existence of two possible scenarios with regards to its consumption:

- the oxygen lowers the methane production because of a partial oxidation of readily biodegradable substrate or
- the oxygen increases the biodegradability of compounds, which are nondegradable or slowly degradable under fully anaerobic conditions.

The following laboratory and full-scale experiments were carried out in order to enhance the understanding of oxygen role in the anaerobic digestion process.

MATERIAL AND METHODS

Analytical procedures were carried out according to the Standard Methods (APHA 2005), biogas composition and volatile fatty acids were determined by gas chromatography. Concentration of AOX was determined using AOX analyser LTX-2000 (Labtech, Czech Republic), in accordance with the standard method ISO 9562 (shaking procedure).

The full-scale experiments were carried out in anaerobic mesophilic digesters of two municipal wastewater treatment plants. Their general technological parameters are presented in Table 1. The air was pumped into the sludge recirculation stream of the digesters (Jenicek et al. 2007).

The additional laboratory experiments were performed in two laboratory digesters (volume 11 L). The first reactor was operated as a microaerobic digester, the second one as a fully anaerobic reference digester. The digested material was a mixture of thickened surplus activated sludge with addition of bone flour to increase the biogas production; both materials are characterized in Table 2.

Table 1 | The technological parameters of the full-scale digesters and the average results before the implementation of microaeration

Digester	A	B
Volume (m ³)	2 * 1500	2,100
Biogas production(m ³ /d)	1,220	830
Hydraulic retention time (d)	25	23
H ₂ S in biogas (mg/m ³)	4,380	7,580

Table 2 | The general characteristics of the material treated in the laboratory digesters

	Activated sludge (g/l)	Bone flour (g/g)
COD	48.8	1.38
CODsoluble	1.83	–
TS	45.74	0.965
VS	29.57	0.671

The mass ratio activated sludge: bone flour was about 50:1. Despite the low concentration of hydrogen sulphide in the biogas, the effect of the air dosing was tested in order to find out the influence of the oxygen in cases where the sulphide oxidation is negligible.

RESULTS AND DISCUSSION

The efficiency of H₂S removal from biogas

During several years of operation of microaerobic desulphurization in the digester A, the efficiency was very good and stable—in average of 99.0% (97.1% when short repair period is included). The required limit of the hydrogen sulphide in the biogas (1,000 mg/m³) was exceeded only once during the last 3 years, when the dosing air pump was being repaired. The long term results are shown in Figure 1.

Similar results were achieved in the digester B. However, the wastewater treatment plant was reconstructed several months after the implementation of microaeration and several technological parameters were changed, which led to a change of the raw sludge quality. Therefore, the evaluated

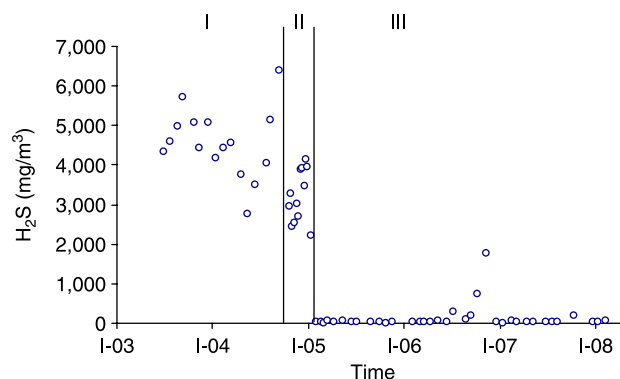


Figure 1 | The course of the hydrogen sulphide concentration in the biogas from the digester A (I—before air dosing, II—start-up of microaerobic period—optimization of the air dose, III—full operation of microaerobic desulphurization).

period is much shorter. The efficiency of the hydrogen sulphide was similarly high (99.1%) regardless of its higher initial concentration (more than 7 g/m³).

Change of other operational parameters

Beside the efficiency of the sulphide removal, the effect on other technological parameters of digestion process is very important for the evaluation of the tested desulphurization technology. The changes of the biogas production and composition and the composition of the digested sludge and the sludge liquor are crucial from the technological point of view.

The efficient biogas desulphurization brings the improvement of the digestion process, which is illustrated in Table 2. The decrease of the relative methane content in biogas is caused by the presence of nitrogen remaining in the biogas from the dosed air. In the digester B, the decrease was even lower than expected, because it was compensated by the higher biogas production.

It is of a high importance that the sludge degradation is deeper in both cases, which is documented by the lower VSS/TSS ratio of the digested sludge. At the same time, the specific biogas production in the digester A is practically unchanged and even increases in the digester B. There is a

certain probability that a part of the VSS is oxidized by the surplus oxygen in the digester A. On the other hand, both the efficiency of sludge degradation and the specific biogas production increased in the digester B, probably thanks to a suppression of the sulphide inhibition of the methanogenic bacteria (Table 3).

It is noteworthy that a significant decrease of the soluble COD concentration was observed, which cannot be explained by a VFA decrease only, it causes about 30 mg/l in digester A and about 120 mg/l in digester B. It is possible to suppose that microaerobic condition stimulated the degradation of slowly biodegradable compounds in sludge liquor (Johansen & Bakke 2006).

Role of the oxygen at the low sulphide concentration

In the subsequent laboratory experiments the influence of oxygen on the digestion at low sulphide concentration (hydrogen sulphide concentration in biogas was below 50 mg/m³) was evaluated. Two digesters were operated at the same conditions for about 3 months in order to achieve a steady state operation. The conditions were then transferred to microaerobic by dosing of the air in one of the digesters. The flow rate of the air was set up at 10% of the actual biogas production.

Table 3 | The influence of the microaerobic sulphide oxidation on the operational parameters of the full-scale digesters A and B

	Before air dosing	After air dosing
Average parameter-digester A		
Ratio O/S ²⁻ *	–	3.7
H ₂ S (mg/m ³)	4,380	41
CH ₄ (%)	65.8	64.5
Specific CH ₄ production (m ³ /t VS added)	314	305
Digested sludge VSS/TSS (%)	56.6	54.6
Soluble COD (mg/l)	430	337
Average parameter-digester B		
Ratio O/S ²⁻ *	–	5.5
H ₂ S in biogas (mg/m ³)	7,580	72
CH ₄ in biogas (%)	65.9	65.4
Specific CH ₄ production (m ³ /t VS added)	201	301
Digested sludge VSS/TSS (%)	65.8	59.7
Soluble COD (mg/l)	778	522

*Only S²⁻ contained in biogas is taken into account.

Table 4 | The comparison of the microaerobic and anaerobic digesters' technological parameters and biogas production

Digester	Microaerobic	Anaerobic
Dose of air (L/d)	1.1	–
Temperature (°C)	40	40
Hydraulic retention time (d)	25.2	25.2
Volumetric loading rate (kg/m ³ .d) (COD)	3.5	3.5
Biogas production (L/d)	10.94	10.97
CH ₄ in biogas (vol.%)	66.7	70.8
H ₂ S in biogas (mg/m ³)	2.6	34
Specific biogas production (m ³ /kg) (COD)	0.37	0.37
Specific methane production (m ³ /kg) (COD)	0.24	0.26

The results in Table 4 confirm that the presence of a limited amount of oxygen in the digester does not destroy the digestion process even in the system where the oxygen is not consumed by prompt sulphide oxidation. Most of the oxygen was probably consumed for organic matter oxidation and therefore the methane production was slightly lower. A slight inhibition of methanogens cannot be excluded, because the dose of the air was relatively high. The biogas production was almost equal, because the missing methane was partly replaced by the nitrogen from the dosed air. The decrease of the methane content in the biogas was lower than expected, due to the surplus nitrogen from the dosed air.

The sludge analyses showed that in all parameters the sludge from microaerobic digester had lower values see Table 5. It means that the total amount of the stabilized sludge produced is lower. Moreover, due to the higher

content of the inorganic fraction in the sludge its dewaterability is supposed to be better. The results confirmed that the degradation of the organic material is slightly deeper in the microaerobic digester.

The quality of the liquid phase is also very important, especially when its further treatment is necessary. The difference in concentrations presented in Table 6 is not significant; however, slightly lower values were measured in the microaerobic conditions again. It is evident that about 7% lower COD concentration was not caused by the lower content of readily biodegradable compounds such as acetate, propionate or other volatile fatty acids salts, but probably due to the degradation of compounds, which are resistant to degradation under fully anaerobic conditions.

AOX biodegradability

Because of the strict concentration limits of AOX (adsorbable organically bound halogens) in the stabilized sludge,

Table 5 | The comparison of the digested sludge quality from microaerobic and anaerobic digesters

Digester	Microaerobic	Anaerobic
TS (g/L)	45.54	46.92
VS (g/L)	25.23	26.44
DS* (g/L)	4.89	5.05
VDS [†] (g/L)	2.20	2.54
TSS (g/L)	40.65	41.87
VSS (g/L)	23.03	23.91
VSS/TSS (%)	55.4	56.4

*DS—dissolved solids.

[†]VDS—volatile dissolved solids.

Table 6 | The comparison of the sludge liquor quality from microaerobic and anaerobic digesters

Digester	Microaerobic	Anaerobic
pH	7.52	7.49
COD-soluble (mg/L)	2,754	2,969
Acetate (mg/L)	29	26
Propionate (mg/L)	13	8
N _{ammon} (mg/L)	2,055	2,100
P-PO ₄ ³⁻ (mg/L)	81.9	97.8

Table 7 | The concentration of AOX in the digested sludge expressed in mg per kg of dry solids

Type of sludge	AOX (mg/kg)	
	Average	Standard deviation
Microaerobic	353	40
Anaerobic	510	52

which is to be applied in agriculture, this parameter was also monitored. The preliminary result seems to be promising, showing that during the two month monitoring of the AOX content in the digested sludge, the average concentration of the AOX in the sludge from the microaerobic digester was 30% lower in comparison with the anaerobic digester. The results are summarized in [Table 7](#).

Such results are interesting especially when according the EU legislation, limit of the AOX concentration for the agricultural use of the stabilized sludge is 500 mg/kg. Considering the presented results, it can be concluded that the presence of oxygen or microaerobic conditions has a positive effect on the biodegradability of the organic compounds determined as AOX. However, more detailed experiments should be carried out in this field.

CONCLUSION

The results of laboratory and full-scale microaerobic experiments can be summarized as follow.

- The application of the microaerobic conditions is an efficient method of the hydrogen sulphide removal from the biogas.
- The efficiency of the hydrogen sulphide removal from biogas of about 99% is a realistic value at a high initial concentration (4,000–8,000 mg/m³).
- The application of the microaerobic conditions is an efficient method of the sulphide toxicity suppression.
- The presence of the limited amount of oxygen in the digester does not destroy the digestion process even in the systems where the oxygen is not consumed by prompt sulphide oxidation.
- The decrease of the methane content in the biogas is lower than expected, due to the presence of surplus nitrogen from the dosed air.

- The VSS/TSS ratio of the digested sludge decreased in all experiments with the microaerobic conditions, due to the better efficiency in VSS degradation.
- A decrease of the soluble COD concentration, ammonia nitrogen and phosphate concentration in the sludge liquor was observed in systems where the microaerobic conditions were applied.

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REFERENCES

- APHA 2005 *Standard Methods for the Examination of Water and Wastewater*, 21st edition. AWWA, Washington, DC.
- Buisman, C. J. N., Geraats, S., Ijspeert, P. & Lettinga, G. 1990 Optimization of sulphur production in a biotechnological sulphide removing reactor. *Biotechnol. Bioeng.* **35**, 50–56.
- Eriksen, N. T., Nielsen, T. M. & Iversen, N. 2008 Hydrogen production in anaerobic and microaerobic *Thermotoga neapolitana*. *Biotechnol. Lett.* **30**, 103–109.
- Janssen, A. J. H., Lettinga, G. & de Keizer, A. 1999 Removal of hydrogen sulphide from wastewater and waste gases by biological conversion to elemental sulphur, colloidal and interfacial aspects of biologically produced sulphur particles. *Colloids Surf. A Physicochem. Eng. Aspects* **151**, 389–397.
- Jenicek, P., Smejkalova, P. & Horecky, P. 2005 Biological microaerobic sulphide removal with respect to specific biomass activity. Proc. of Int. Conf. Anaerobic Digestion of Solid Wastes, Copenhagen. 145–148.
- Jenicek, P., Smejkalova, P., Pokorna, D., Zabranska, J. & Dohanyos, M. 2007 The improvement of anaerobic digestion efficiency by microaerobic sulphide removal—full scale experience, CD-proc. of 11th Int. Conf. on Anaerobic Digestion, Brisbane.
- Johansen, J.-E. & Bakke, R. 2006 Enhancing hydrolysis with microaeration. *Water Sci. Technol.* **53**(8), 43–50.
- Khanal, S. K. & Huang, J. C. 2003a Anaerobic treatment of high sulfate wastewater with oxygenation to control sulphide toxicity. *J. Environ. Eng.* **129**, 1104–1111.
- Khanal, S. K. & Huang, J. C. 2003b ORP-based oxygenation for sulfide control in anaerobic treatment of high-sulfate wastewater. *Water Res.* **37**, 2053–2062.
- Krishnakumar, B., Majumdar, S., Manilal, V. B. & Haridas, A. 2005 Treatment of sulphide containing wastewater with sulphur recovery in a novel reverse fluidized loop reactor (RFLR). *Water Res.* **39**, 639–647.

- Noparatnaraporn, N., Sasaki, K., Nishizawa, Y. & Nagai, S. 1986 Simulation of vitamin B12 formation in aerobically-grown *Rhodospseudomonas gelatinosa* under microaerobic condition. *Biotechnol. Lett.* **8**(7), 491–496.
- Pitter, P., Sykora, V. & Kral, P. 2005 The problems with interpretation of the results of oxidation-reduction potential (ORP) measurement. *Vodni hosp.* **55**(5), 134–135, (in Czech).
- Tang, Y., Shigematsu, T., Ikbai, Morimura, S. & Kida, K. 2004 The effects of micro-aeration on the phylogenetic diversity of microorganisms in a thermophilic anaerobic municipal solid-waste digester. *Water Res.* **38**, 2537–2550.
- van der Zee, F. P., Villaverde, S. & Garcia, P. A. 2007 Sulfide removal by moderate oxygenation of anaerobic sludge environments. *Bioresour. Technol.* **98**(3), 518–524.
- Zacharias, B., Lang, E. & Hajery, H. H. 1995 Biodegradation of chlorinated aromatic hydrocarbons in slow sand filters simulating conditions in contaminated soil-pilot study for in situ clearing of an industrial site. *Water Res.* **29**(7), 1663–1671.