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Analytical Methods for the Determination of the Biological Activity of MSW

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Abstract
Determination of the biological stability of waste samples is presented for selected methods with respect to the verification of biodegradability, which are applied at the Institute of Waste Resource Management of the Hamburg University of Technology. These methods serve to ascertain the respiration activity (RA_4), the gas formation potential (GP_{21}), the gas generation sum (GS_{21}) and the dynamic respiration test (DR_4). The possibilities and limitations of the individual test methods could be shown by comparing the different methods (supported by selected results of the investigation).

1 Introduction
To reduce warming of the earth's atmosphere, the Member States of the European Union have undertaken to reduce the emission potential of landfills. The EU Landfill Directive dated April 26th 1999 (Council Directive 1999/31 EC), which was created for this purpose, stipulates different measures in order to achieve this target. In this respect, the reduction of the deposition of biodegradable waste represents the essential point, connected with an effective gas control for landfills. The requirements stipulate a progressive reduction by 65% of the amount of biodegradable waste to be deposited by 2016. Varying measures are implemented in the individual Member States of the EU to achieve this aim. In Germany, for example, all amounts of waste to be deposited need to be pre-treated in order to reduce the emission potential of the biodegradable fraction. The respective criteria are specified in the German Ablagerungsverordnung. To check compliance with these parameters, waste samples are to be taken and analysed at regular intervals. Amongst others, the respiration activity (RA_4) or the gas formation potential (GP_{21}) need to be determined for the description of biological stability (see Table 1). In Germany, standard requirements are defined for the implementation of these analytical methods. In other EU Member States it is implemented differently. Consistent European standardised methods for the determination of the biological stability of waste samples do not exist.

In the following, different methods for the determination of the biological

stability, which are applied at the Institute of Waste Resource Management of the Hamburg University of Technology, are introduced and their possibilities and limitations are described and discussed. In the long term, the aim should be to harmonise the methods used for the description of the biological stability of waste, at least throughout Europe. Where required, a modular standardised concept could be developed.

2 Material and methods

The following test methods for the determination of the biological stability of waste samples were applied within the scope of research and development projects and in comparative round robin studies (national / international):

- Determination of the respiration activity in 4 days (RA_4, aerobic)
- Determination of the dynamic respiration test in 4 days (DR_4, aerobic)
- Determination of the gas formation potential in 21 days (GP_{21}, anaerobic)
- Determination of the gas generation sum in 21 days (GS_{21}, anaerobic)

Via these test methods, the behaviour of waste under landfill conditions shall be determined within a short period of time using standardised methods. The individual methods for the determination of the biological stability may be divided into aerobic and anaerobic test methods. Determination of the RA_4 respiration activity and of the dynamic respiration test (DR_4) is implemented under aerobic milieu conditions, determination of the GP_{21} gas formation potential and of the GS_{21} gas generation sum under anaerobic conditions. Methods RA_4, GP_{21} and GS_{21} are to be applied for the assessment of the biological reactivity of mechanically-biologically treated waste. The DR_4 is also a suitable test method to determine the biological reactivity of non-treated sample materials, which show a higher biodegradation potential. For the assessment of non pre-treated waste, the RA_4, GP_{21} and GS_{21} methods need to be modified correspondingly.

It applies to all investigation methods that, subsequent to representative sampling, the waste to be examined needs to be prepared using standardised methods. As a rule, sample materials with a diameter of d<10mm are to be investigated in the test systems. For this purpose, samples are to be screened and ground before hand, where required. For preservation, sample materials are to be frozen. With respect to DR_4 determination, the material also needs to be pre-dried at a temperature of T=70°C.

2.1 Determination of respiration activity in 4 days (RA_4)

RA_4 respiration activity may be determined in the respirometer (Sapromat, produced by IBUK, Germany) or in a batch test using pressure sensors (Oxytop, produced by WTW, Germany). In both test systems, the carbon dioxide produced by microorganisms is bonded to soda lime. As a result, negative pressure develops. The oxygen consumption is determined stoichiometrically. From time to time the negative pressure has to be released. The Sapromat works in a similar manner where the CO_2 produced also is absorbed by a base so that a negative pressure

builds up. A sensitive pressure sensor gives a signal to an electrolytical oxygen production cell which produces oxygen until the pressure is "neutral". Compared with the pressure sensor system, the Sapromat has the advantage that oxygen which is consumed by microorganisms is immediately supplied electrochemically and thus, oxygen limitation usually may not occur (maximum O_2 production approximately 25 mg O_2/h). Depending on the activity of the sample materials, the batch tests with the pressure sensors need to be opened at certain time intervals and rinsed using air or oxygen. The weighed-in quantity of the sample material amounts to up to 50 g WM for mechanically-biologically treated waste (triple preparation). Prior to that, the sample materials need to be adjusted to optimum moisture content. The latter lies between 50% and 70% of the maximum water holding capacity (WHC) of the sample and is controlled via the "vacuum suction filter method" respectively determined using the so-called "Faustprobe" (method originally developed to adjust the moisture content). During the investigation period of at least 4 days, the ambient temperature is kept at T=20°C.

2.2 Determination of DR_4 dynamic respiration test

With respect to the DR_4 method, which is standardised in the UK (Environment Agency, 2005), and in contrast to the RA_4 determination, the material is submitted to forced aeration in 2-3 litre reactors. Subsequently, the oxygen consumption or the carbon dioxide production is determined. Measurement of the carbon dioxide concentration may be implemented via wet-chemical methods (titration) or via IR or GC analysis. A sufficient oxygen supply is ensured through high aeration rates, so that even materials with a high biological activity may be examined.

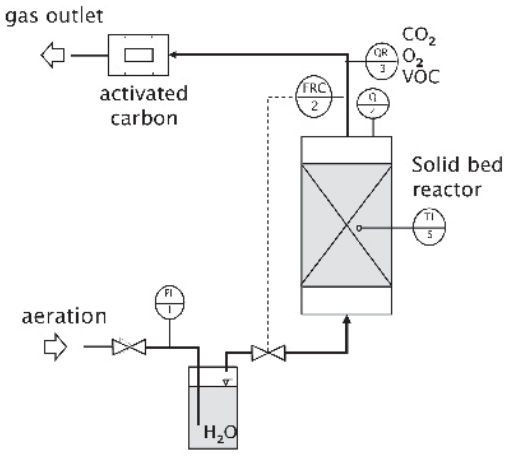


Fig. 1: Principal scheme of the static bioreactors at the Hamburg University of Technology for the determination of the Dynamic Respiration test (DR_4).

Regarding the DR_4 method, and in contrast to the RA_4 determination, a larger amount of waste sample (100 g DM = dry matter) is analysed in order to take into account possible inhomogeneities in the sample material.

The sample material is additionally spiked with fully matured compost as an inoculant. The suitability of the inoculating agent may be ascertained in an additional test using cellulose as a reference material. The functionality of the test system is checked in a blank test. Ambient temperature for the DR_4 method is T=35°C and the duration time is 4 days. Figure 1 describes the principal scheme of the test system used at the Hamburg University of Technology, following the DR_4 method.

2.3 Determination of GP_{21} gas formation potential

With regard to the GP_{21} method, the gas formation potential of mechanically-biologically treated sample materials may be determined volumetrically using an eudiometer (developed at the TUHH) or manometrically using pressure sensors (Oxytop, WTW, Germany). The material to be analysed (50 g WM = wet matter) is examined with digested sewage sludge and water over a period of at least 21 days at an ambient temperature of T=35°C. The digested sewage sludge is tested in a reference preparation using cellulose (Avicell). In order to ensure a tested anaerobic process, the free gas volume of the reactor is rinsed using nitrogen. In addition, the pH value milieu is measured at the beginning and at the end of the investigation. In the eudiometer, the gas production is determined manually per working day; in the manometric test system, the data are stored discontinuously and may be read out via an IR interface for further evaluation purposes. The gas production ascertained in the test is given in l_{std}/kg DM, based on standard conditions.

2.4 Determination of the gas generation sum GS_{21} in 21 days

Determination of the GS_{21} gas generation sum differs from GP_{21} mainly by the amount of material to be analysed (800 - 1500g DM), the water balance to be adjusted (100 % water holding capacity max.). No inoculating material is used in this test. The water-saturated sample material is placed onto a screen at the bottom in a 2.5 - 3 litre reactor. The gas production is measured using an eudiometer. At the Institute of Waste Resource Management of the TUHH, biogas production is determined volumetrically using a revolving-drum meter (produced by Ritter, Germany). To ascertain the gas composition, gas samples may be taken and submitted to gas chromatographic analysis (GC-WLD, HP) with regard to the parameters CH_4, CO_2, N_2, O_2 and H_2. The pH value needs to be analysed at the beginning and at the end of the investigations. The temperature of the water bath is set to T=40°C. In section 3, the applicability of the presented test systems is described by means of selected examples. Table 1 shows a summary of the characteristic features of the determination methods.

3 RESULTS AND DISCUSSION

3.1 Characterisation of mechanically-biologically pre treated waste via the determination of RA_4 and GP_{21}

In Germany and in Austria, methods for the determination of RA_4 respiration

Tab. 1: Selected methods for the determination of the biological stability of waste samples

Test method	**RA_4**	**DR_4**	**GP_{21}**	**GS_{21}**
Milieu conditions	aerobic	aerobic	anaerobic	anaerobic
Sample preparation	d<10mm	Drying at T=80°C grinding d<10mm	d<10mm	d<10mm
Gas analysis	O_2 consumption CO_2 production continuous manometric	O_2 consumption or CO_2 production continuous titration, O_2-analyser or CO_2-analyser	gas production, optional CH_4, CO_2 working day manometric, volumetric	gas production, optional CH_4, CO_2 working day volumetric
Test period	min. 4 days	min. 4 days	min. 21 days	min. 21 days
Water content in the reactor	50 - 70% of WHC	50 % (w/w)	8 - 10 % (w/w)	100% of WHC
Temperature	20°C	35°C	35°C	40 °C
Amount of test material	30 – 50 g WM	100 g DM	50 g WM	800 - 1500g DM
Seed material	no	yes	yes	no
Reactor volume	500 – 2500 ml	2500 - 3000 ml	500 ml	2500 - 3000 ml
Reference set up	no	yes	yes	no
Unit	[mg O_2/g DM]	[mg O_2/g DM]	[l_{std}/kg DM]	[l_{std}/kg DM]

WHC: Water holding capacity

activity and of GP_{21} gas formation potential are applied as standardised test methods for the assessment of mechanically-biologically pretreated waste. In Germany, the limit values for RA_4 lie at 5 mg O_2/g DM and at 20 l_{std}/g DM for GP_{21}. For the characterisation of the emission potential, RA_4 or GP_{21} may be determined alternatively. Priority usually is given to the determination of RA_4, as a period of 4 days for the determination of the analysis value is significantly shorter than those 21 days which are required for GP_{21}. Furthermore, implementation of the GP_{21} test method is more complex and thus more costly.

As already described in sections 2.1 and 2.3, both investigation methods may be implemented using different test systems. RA_4 may be determined in the Sapromat (respirometer) or in the Oxytop system, GP_{21} in the reactor with an eudiometer or in the Oxytop system. Comparability of the results of both test systems was confirmed in different investigations (Robertz et al., 1997; Heerenklage and Stegmann, 2001).

In order to measure RA_4 respiration activity of non-treated waste samples with a high biological activity, weighed-in waste samples with less than 50 g WM may

be used, where required, in order to ensure a sufficient oxygen supply. Sample materials showing an increased activity, the Oxytop system is suitable only with some reservations, as continuous opening for air exchange purposes leads to measurement inaccuracies.

Compared with the eudiometer, the Oxytop system shows disadvantages at higher gas production rates as far as the determination of GP_{21} gas formation potential is concerned, as a maximum overpressure of 350 mbar may be measured. Subsequently, the gas is released from the Oxytop system in order to ensure accurate measurement. Where required, this could be automated in the future by using pressure relief valves. Compared with the eudiometer, the manometric test system has small advantages with regarding to gas tightness, as further connection hoses will not be required. Viton tubes have proven particularly suitable in the eudiometer as far as gas tightness is concerned. Checking the gas tightness of anaerobic test systems is of special importance. In this respect, a nitrogen / carbon dioxide gas mixture should be applied, as carbon dioxide diffuses through various materials. The tightness check with pure nitrogen could simulate system tightness. Investigations carried out by Müller (2002) have shown that the selection of the liquid in the eudiometer also exerts an important influence on the determination of the gas production. The barrier effect of a solution of a NaCl/citric acid against the dissolving behaviour of CO_2 is significantly higher than, for example, an H_2SO_4 solution with a pH below 3. The Na_2SO_4/H_2SO_4 liquid given for GP_{21} determination also boasts very good barrier properties. According to the provisions, digested sewage sludge from a municipal sewage treatment plant with a dry mass of 5% should serve as inoculum. The latter should be stored at T=35°C and show only a low gas production. Anonymus (2004) suggests the general use of a digested sludge solid content with an organic mass of 1.5 to 2% (w/w) for the implementation of fermentation tests. The ratio in GP_{21} is 50g WM of sample material: 50 ml of digested sludge with 300 – 400 ml of water. This also corresponds to the recommendations of the VDI 4630 draft (Anonymus 2004) which defines a ratio of $oDS_{substrate}$: $oDS_{digested\ sludge}$ of below 0.5. In this respect, the gas production of the substrate should amount to more than 80% of the total gas production of a sample. In the reference set-up (weighed portion 1g of cellulose), at least 400 ml_{std} of biogas should be produced in order to classify the activated sludge as suitable.

3.2 Determination of GS_{21} gas generation sum for the characterisation of biologically pre-treated waste

Compared with the GP_{21} test, considerably larger sample portions are used for the determination of GS_{21} gas generation sum. With sample volumes between 800 and 1500 g DM for GS_{21} (compared with 50 g WM for the determination of GP_{21}), inhomogeneities in the sample material may be compensated, where required. In contrast, the test is more complex. As no inoculating agent is added, extended lag phases may occur at the beginning of the investigations and result in extended

investigation periods. In an extreme case, this may lead to sustained acidification of the system and to lasting inhibition of the gas production. To avoid this, leachate should be circulated in the case of acidification and the pH value should be raised to a neutral range via careful addition of a buffer solution. With respect to materials with an increased biological activity, the GS_{21} method is suitable only to a limited extent. Comparative investigations confirmed the reproducibility of GP_{21} and GS_{21} investigations for mechanically-biologically treated materials.

3.3 Determination of biodegradability via the DR_4 dynamic respiration test

In contrast to RA_4 test, analysis of the dynamic respiration test (DR_4) is carried out using significantly larger amounts of test material (100g DM in the DR_4, compared with 50 g WM (approximately 20-25 g DM) in RA_4). Existing inhomogeneities in the waste may be better compensated. The test temperature is 35°C, in order to create the same conditions which were used for the measurement of the gas formation potential. Different from the RA_4 test, the DR_4 also serves to analyse fresh waste samples with high oxygen consumption. Therefore, the individual reactors are aerated with a high aeration rate of 2.5 L/(kg DM min) (i.e. 500ml air/min). In time, our own investigations in accordance with the provisions of the DR_4 set-up will be carried out at the TUHH. In the past the test system has proven particularly suitable for these investigations and also meets the requirements for the DR_4 set-up (Lotter et al, 2001; Heerenklage a. Stegmann, 1997). The addition of an inoculating agent to the test material with a high proportion of biodegradable compounds (1:1 (w/w)) is to counteract possible early acidification in materials showing high biological activity (kitchen waste). Furthermore, sufficient organic mass for the verification of biodegradability may be supplied to test material with insufficient biomass (such as a mono batch of waste paper). The inoculating material itself is also tested (similar to GP_{21} investigations) with regarding to its suitability using a reference substance. In the following, investigations regarding the application of inoculating agents in a modified RA_4 test system are presented. The result of the DR_4 investigations (similar to RA_4) carried out over a period of 4 days is given as the total oxygen consumption per weight of the test material [mg O_2/kg DM respectively mg O_2/kg oDM].

3.4 Application of inoculating materials for the verification of biodegradability during the RA_4 determination in the Sapromat

As already mentioned, an inoculating agent is added to the test material to be analysed using the DR_4 method. In preliminary tests, the influence of the inoculating agent was also tested in a modified RA_4 determination in the Sapromat. Biological activity of kitchen waste was analysed within 4 test days (see Figure 2). In three different set-ups, kitchen waste, kitchen waste including an inoculating material, and the inoculating material itself were tested. With respect to the "kitchen waste" set-up, biological activity could be ascertained only after a period of approximately 120 hours. Subsequently, oxygen consumption increased sharply. If the test had ended after the prescribed 4 test days (96 h), no oxygen

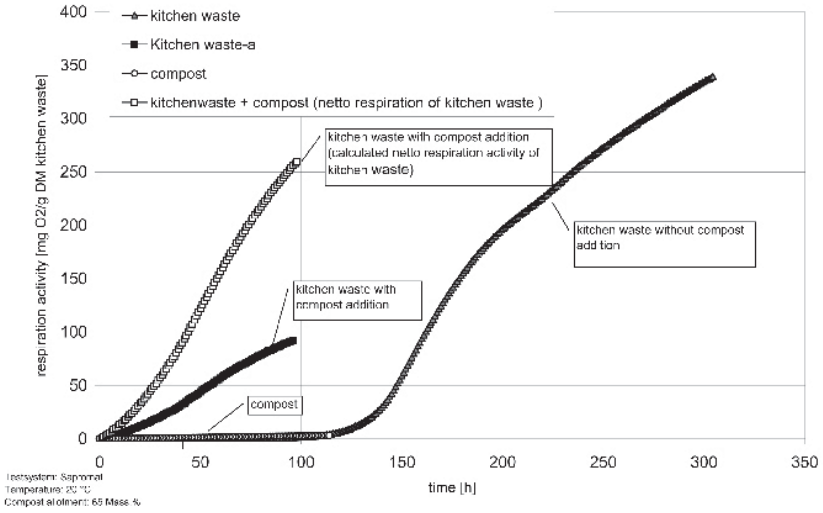


Fig. 2: Influence of the addition of compost on the lag phase of materials with an increased biological activity

consumption by the kitchen waste would have been measured. In the competitive experiment including the addition of fully matured compost (compost portion of 65% (w/w)), a respiration activity of 70 mg O_2/g DM was measured after 4 days. The oxygen consumption of the investigated compost material amounted to 2.6 mg O_2/g DM in the same period of time. By calculation a respiration activity of 256 mg O_2/g DM was determined for pure kitchen waste.

It is likely, that the inhibition of the respiration activity at the beginning of the investigations with pure kitchen waste is attributable to the pH value. For kitchen waste, a pH value of pH=6.4 was measured and the kitchen waste / compost mixture showed a pH of pH=7.5. When determining the respiration activity for the "kitchen waste" set-up by means of a correction by the lag phase, oxygen consumption amounts to 232 mg O_2/g DM after 4 days. The end of the lag phase was defined at 25% of the maximum conversion rate (6 hourly mean values) and amounts to 126 hours. Both respiration activities (RA_4) show for kitchen waste (including and excluding the addition of an inoculating material) more or less the same results. Determination of RA_4 respiration activity of materials with an increased biological activity should therefore be implemented using an inoculating agent in order to counteract inhibition of the activity.

4 Conclusions

Determination of the biological stability respectively the biological activity of waste samples was introduced using selected test methods, which are applied at the Institute of Waste Resource Management of the Hamburg University of Technology. These methods serve to determine the respiration activity (RA_4), the gas formation potential (GP_{21}), the gas generation sum (GS_{21}) and the dynamic respiration test (DR_4). By way of comparison of the different methods and by means of selected findings, possibilities and limitations of the individual test methods could be shown. RA_4 and GP_{21} investigations are suitable for the determination of the biological stability of mechanically-biologically pre-treated waste materials. Via the addition of compost as the inoculating agent, materials with an increased biological activity and waste compounds without a distinct biomass may also be investigated. The RA_4 and GP_{21} determination methods can be considered equivalent with respect to the results gained. However, determination of the gas formation potential requires more work and time. Compared with the Oxytop system, the Sapromat has advantages as far as the RA_4 method is concerned, as normally no oxygen limitation will occur. The volumetric determination method of the gas production also has advantages compared to the Oxytop system, as higher specific biogas rates may be analysed as a result of the limitation by the pressure sensor. Via increased addition of the inoculating material, non-pretreated waste may also be investigated. The method for the determination of the dynamic respiration test also enables the description of waste samples showing high biological activity. In addition larger waste compound volume without own biomass can be investigated using adequate amounts of an inoculum. Due to the sample (compared with the RA_4 determination), inhomogeneities in the material may be compensated. However, as far as the determination of the degree of biodegradation is concerned, the technical requirements are significantly higher. Compared with the GP_{21} method, the measurement of the biogas production via the GS_{21} gas generation sum has the advantage that the sample volume to be applied is considerably larger. In this manner, inhomogeneities in the material may also be compensated. The gas production of mechanically-biologically pre-treated waste sample materials may be determined within a period of 21 days. Regarding materials showing increased activity, an extended lag phase can be assumed, which should be avoided.

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