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INVESTIGATION OF DAILY COVERING MATERIAL FOR BIOCELLS

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Bioreactor landfilling, with the acceptance of landfill Directive 1999/31/EC has lost its actuality in European Union; at the same time, this method can still be used for acceleration of biowaste degradation and biogas production. One of the possibilities to reduce the disposal of biowaste is to use biocells for its anaerobic pre-treatment before landfilling. The daily filling up of such a cell requires isolation of the main volume to limit gas emissions, reduce smells, etc. Bioprocesses that are of the utmost importance for biocell treatment are often not taken into account in selection of materials to be used as daily landfill covers. Based on physical, chemical and biological methods the investigations have been carried out into different covering materials offered in the market, with identification of parameters that are the most important for daily covering the biocells. It is found that the materials fitted best this purpose should be of biological origin and consist of small bio-particles with large surface, without the inhibitors of anaerobic processes such as sulphuric compounds.

Keywords: *landfilling, bio (reactor) cells, daily covering materials, anaerobic bioreactions, chemical composition of materials.*

1. INTRODUCTION

Nowadays, among the disposed waste in the sanitary landfills of Latvia the biodegradable waste composes ~ 50 %, and its degradation produces ~ 8 % of the total greenhouse gas emitted in the country (recalculated to CO_2) [1]. The main problems in promotion of the waste disposal are large amounts of unsorted waste and low effectiveness of the sorting lines [2]. At anaerobic treatment with optimal conditions for biowaste putrefaction it was revealed that the poorly sorted waste cannot be used at traditional facilities for biogas production.

The idea of designing separate closed biocells for the waste treatment is not something new; however, practical realization of such biocells poses many problems, especially as concerns selection of the daily covering material.

The biocell under consideration is designed and operated to reduce risks associated with the produced infiltrates and the emission of landfill gases (mainly

CH_4 and CO_2). In a biocell, the rates of anaerobic processes are much higher than in a conventional landfill. The microbiological decomposition of biodegradable material proceeds there in a shorter time span (1-3 years). Due to increased density of the waste mass, it is possible to save 15 to 30% of the landfill space [3].

The practical usage of covering materials shows that there are differences not only in the price of material and technical operations, but also in the volume of the gas produced. In our investigations we tried for the first time to resolve the practical question – what are to be the main properties of a covering material that would determine the quality of anaerobic processes?

In the anaerobic technology for gradual recycling of biomass, different groups of bacteria are used in a process consisting of the following phases:

1. the *hydrolysis* phase, with splitting of macromolecular organic compounds into smaller components;
2. the *fermentation* phase, with fermentation of acids created in hydrolysis and production of new substances: propionate, butyrate and acetate;
3. the *methane fermentation* phase, in which biogases (methane and carbon dioxide) arise [4].

The effectiveness of anaerobic fermentation depends on several basic parameters, so it is very important to provide adequate conditions for anaerobic microorganisms. Their growth and activity in the absence of oxygen depend also on the temperature and pH value of surrounding environment, nutrient supply, as well as on the presence and concentration of inhibitors. Methanogenic bacteria are highly demanding for anaerobic conditions, thus the presence of oxygen is definitely not to be allowed.

Microelements such as iron, nickel, cobalt, selenium, molybdenum and tungsten are as important as macroelements for the growth and survival of anaerobic fermentation bacteria. The optimal ratio of the macroelements - carbon, nitrogen, phosphorus and sulphur (C: N: P: S) - is 600:15:5:1. Lack of nutrients and microelements as well as too high ability of substrate fermentation can cause inhibition and disturbances of anaerobic fermentation process [4].

2. MATERIALS AND METHODS

The investigation into the properties of daily covering materials was carried out on the covering material received from different companies – i.e. the samples consisting of the main material (filler) and added polymeric material. The fillers for samples were: straw of five types with polymeric material (samples No.1- 5); one sample material from pulped paper (No.6); one spray material – (No.7); two organic glue samples (No.8 and 9).

Chemical analysis of the samples

For the analysis of all samples (No.1 - 9) a variable pressure Schottky-type field emission SEM Mira\LMU was used. A sample was placed on the SEM base, and, using energy dispersive spectroscopy (EDS) the elemental composition was determined in percent.

The powder-wise samples No. 8 and 9 were subject to the X-ray diffraction (XRD) analysis. In this method a polycrystalline sample was irradiated with X-rays at different angles. The phase analysis was performed using PDF-2/2005 database.

For the analysis of chemical bonds in samples a VARIAN 800 FT-IR spectrometer (wave number 400-4000 cm^{-1}, resolution 4 cm^{-1}) was used. For the spectral analysis the samples were prepared in the shape of compressed KBr tablets or disks.

Evaluation of bacterial viability

In the studies of anaerobic fermentation it was found that this process is caused by definite types of bacteria: first of all hydrolytic bacteria, then acidogenic (i.e. acid-forming) bacteria, and, at the last place, some facultative anaerobic and strictly anaerobic metanogenic bacteria (i.e. producing the methane gas). Samples No.1 - 7 were placed in 60-ml containers with 30 ml of inoculum (obtained as digestate) from a working demonstration-scale biogas plant. In each container 0.5 g of a daily covering material was placed.

The containers were left in the incubator for two weeks at 37 ^{o}C, occasionally discharging the produced biogas. Then from each container the samples of digestate were collected to analyze for micro-organisms. Bacteria count in the cell was determined by the DAPI method. The samples were washed using a microporous filter (20 mkm). The microscopy tests were performed by means of an epifluorescence microscope (*Leica DMLB*) equipped with a mercury lamp, filters (Ex: 340-380, Em.> 425 nm, dichromatic mirror 400 nm) and a camera (*CoolSNAP Pro, Media Cybernetics, Inc*., USA). The samples were tested using a 1000x oil immersion objective. The pictures were analyzed with the help of Image-Pro Plus version 4.5 (*Media Cybernetics, Inc,* USA) Windows software.

3. RESULTS AND DISCUSSION

Composition of the samples

Results of the energy dispersive X-ray spectroscopy (SEM EDS) for all materials are shown in Tables 1 and 2, where the main elements and their content (in % of mass) in a sample are presented.

Comparative results for elemental composition of samples No.1 and No.3 (straw + polymeric additive) have shown their similarity, except the absence of Cl and Zn in sample No.3; these elements most likely affect the sensitivity of the polymer material to the moisture facilitating its sliding on slopes. As compared with No.1 and No.3, sample No.2 contains a very small amount of Fe and a significantly higher amount of Al. Sample No.4 has the highest diversity of elements (including those providing the conformity with slopes and other unfavourable soil conditions). The content of samples No.5, 7-9 is similar to that of previous ones. As regards sample No.6 (pulped paper), such elements as C, O, S, Ca were detected in its entire volume, with the sulphur content from 0.33% to 34.25 %. The high concentration of Ca ions indicates that in the paper production $CaCO_3$ was possibly used. It can also be seen that the sample has sulphur compounds, which means that such recycled paper material is not suitable for biogas production, as these compounds might be released at the contact with biomass and inhibit the synthesis of biogas as well as generate hydrogen sulphide biogas – a polluting substance which is difficult to separate.

Table 1

Content of the main elements (C, O, Na, Mg, Al, Si, P) in different samples (% of mass)

	C	O	Na	Mg	Al	Si	P
(1)Max	69.2	49.5	0.2	1.7	1.7	22.2	0.6
(1)Min	22.1	25.3	0.2	0.1	0.1	0.4	0.1
(2)Max	71.1	57.9	2.8		9.1	26.8	
(2)Min	10.7	25.3	1.9		0.6	2.3	
(3)Max	72.1	51.9	0.7	0.7	2.4	29.7	0.3
(3)Min	17.9	19.0	0.6	0.3	0.1	0.3	0.3
(4)Max	67.2	50.4	0.2	1.8	5.7	13.2	0.6
(4)Min	19.3	29.0	0.1	0.2	0.1	0.4	0.6
(6)Max	72.9	52.8		0.2	2.2	31.5	
(6)Min	15.6	26.5		0.2	2.2	1.1	
(7)Max	56.7	53.8		7.5	2.4	11.2	
(7)Min	11.4	5.4		0.2	0.2	0.2	

Table 2

Content of the main elements (K, Ca, Fe, Cl, Zn, Ti, S) in different samples (% of mass)

	K	Ca	Fe	Cl	Zn	Ti	S
(1)Max	6.4	1.2	24.4				
(1)Min	0.9	0.4	24.4				
(2)Max	1.7	4.5	1.2				
(2)Min	0.2	0.3	1.2				
(3)Max	4.3	0.9	17.2	0.2	0.4		
(3)Min	0.2	0.2	0.3	0.2	0.4		
(4)Max	4.8	2.5	15.9	0.3	0.2	0.6	
(4)Min	0.5	0.4	2.8	0.2	0.2	0.6	
(6)Max	0.7	0.3	0.5				
(6)Min	0.4	0.3	0.5				
(7)Max	0.2	47.9	0.53				34.3
(7)Min	0.2	4.5	0.53				0.3

Results of XRD analysis

Analyzing samples No.8 and No.9 (organic glue) by the X-ray diffraction method described above, a diffractogram was obtained; comparing it to the database entries some crystalline substances were identified: $(NH_4)_2HPO_4$ (added to polymers to reduce their combustibility) in sample No.8, and NaCl (possibly, added as preservative) in sample No.9.

Results of FTIS analysis

Using the Fourier transform infrared spectroscopy (FTIS) the polymer in the samples was analyzed.

The FTI spectra of samples (No.1 – 5, straw + polymer material) are shown in Fig. 1. All the samples contain one type of polymer material, which is characterized by combination and location of spectral bands.

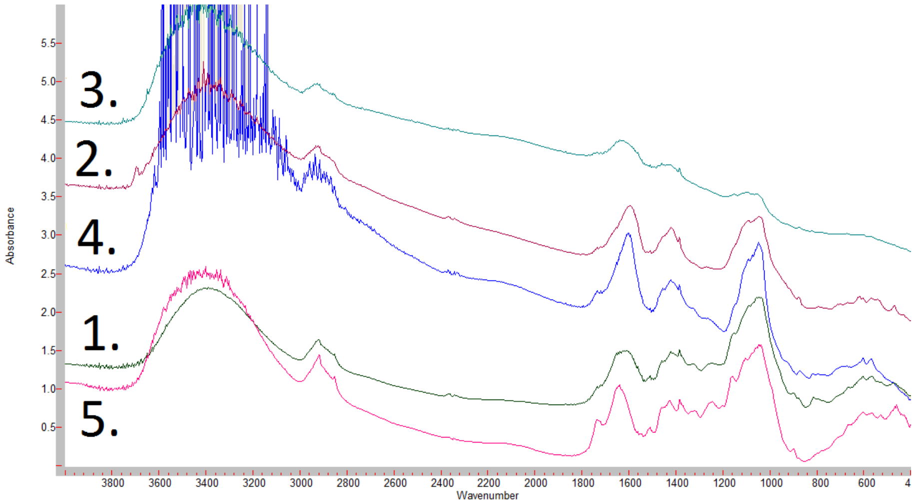

Fig. 1. Fourier transform infrared spectra of samples No.1 – 5

In Fig. 2 FTI comparative spectra of pure Guar Gum and No.1 (straw + polymer material) are shown. The relevant IR absorption bands (wave numbers) of pure Guar Gum and possible chemical groups are presented in Table 3.

Table 3

IR absorption band locations (wave numbers) of the pure Guar Gum and possible chemical groups

Wave numbers of pure guar gum (cm^{-1})	Possible chemical groups	Wave numbers of pure guar gum (cm^{-1})	Possible chemical groups
3550, 3476, 3414	ν_{as} NH_2, ν_s NH_2, H_2O abs., OH	1093	ν_b CC
3230	νs NH_2	1068	* (CO), (CN)
2924	ν CH un CH_2	1035	* (CO), (CN)
2857	ν CH un CH_2	962	* ν_s CC
1740	ν C=O	873	* (C-H)
1638	δ OH	813	CH_2
1618	COO^-, δ NH_2	770	ω (C-H)
Wide band 1350-1480	CH_2, C-OH	710	* (C-H)
1313	CH_2,CH_2OH	605	* (C-H), (C-X)
1258, 1222	CO, SO	567	* (C-X)
1155	ν_b CC	527	* (S-S)

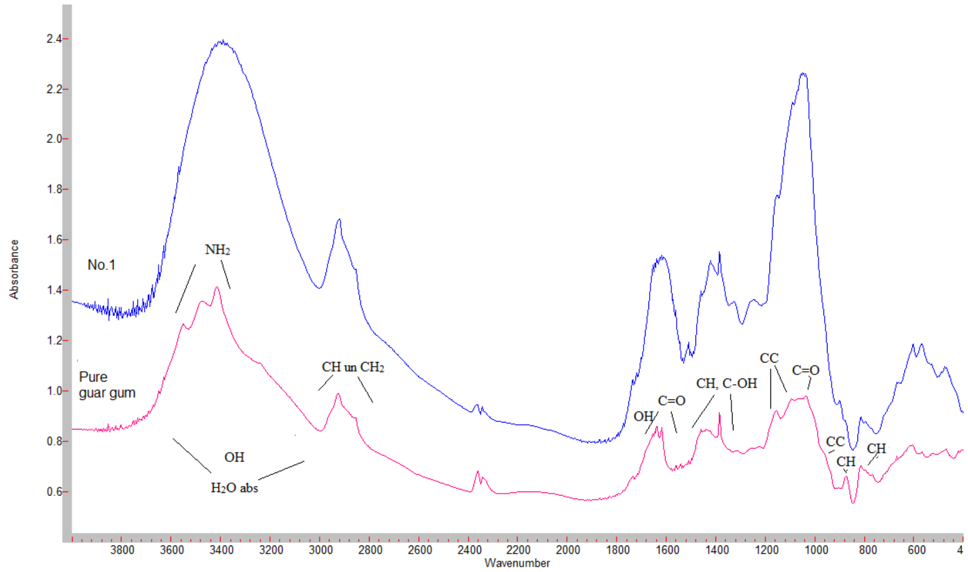

Fig.2. Fourier transform infrared spectra of sample No.1 and pure Guar Gum

The spectra obtained for polymeric materials (samples No.8 and No.9) are displayed in Fig. 3. As is seen, the spectra differ in the characteristic combinations, shapes, intensity and location of the absorption bands, suggesting the existence of other chemical bonds than in sample No.1 or pure Guar Gum.

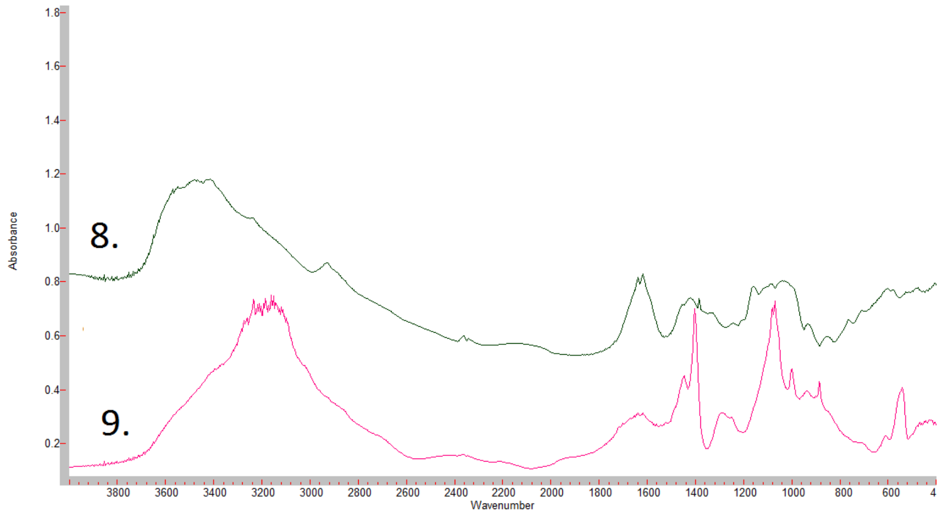

Fig.3 Fourier transform infrared spectra of samples No.8 and No.9.

In Fig. 4 and Table 4 a comparative distribution of spectral bands is shown for samples No.7 and No.8. Locations of their spectral bands as compared with that of the reference material evidence their close similarity; in fact, in the samples all standard characteristic bands of the polymeric material are also observed. Comparing the wave numbers of the FTIR spectra with the data from literature sources, it was found that one of the components is a polymer that most likely is polyacrylamide (C3H5NO)n with acrylamide unit (-$CH_2CHCONH_2$-), as all its characteristic bands were observed.

The analysis was complicated by the fact that the studied samples present a mixture of substances, so spectral lines may overlap; also, it was difficult to get rid of quite a large amount of water whose absorption band appears in the 3000-3600 cm^{-1} range and overlaps with that of NH_2.

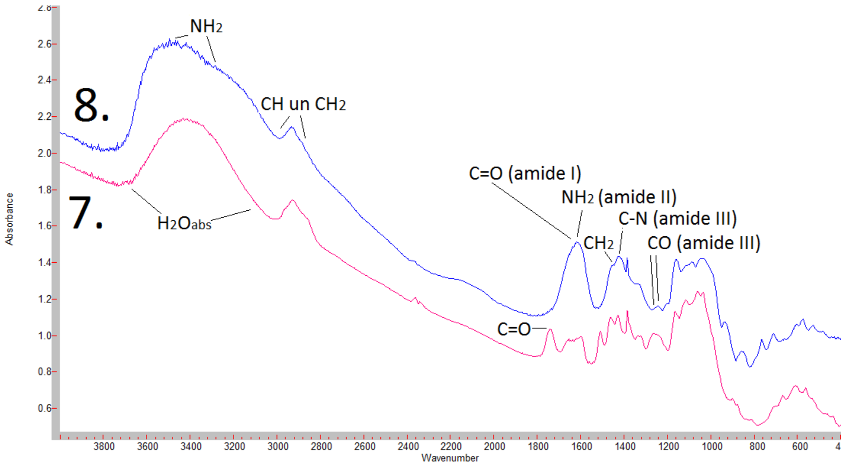

Fig.4. Comparative Fourier transform spectra for samples No.7 and No.8.

Table 4

IR absorption band locations (wave numbers) of samples No.7 and 8 and possible chemical groups

Wave numbers for sample No.7 (cm^{-1})	Wave numbers for sample No. 8 (cm^{-1})	Possible chemical groups
int. 3020- 3690 (3410)	int. 3020- 3690	ν_{as} NH_2, ν_s NH_2, H_2O abs.
(3500, 3200)	OH	
2965	2965	νCH un CH_2
2930	2930	νCH un CH_2
2855	2870	νCH un CH_2
1740	-	ν C=O
1660	int.1710-1550 (1615)	ν C=O (amide I), δ OH
1600	-	δ NH_2 (amide II)
1507	-	
1458	1458	δ CH_2
1428	1422	ν C-N (amide III)
1384	1384	CH_3
1336	1339	ω CH_2
1320		δ CH
1262		CO (amide III)
1244	1244	CO (amide III)
1205	1205	ω NH_2

1163	1163	ν_b CC
1114	1114	* (PO)
1087	1087	ν_b CC
1060	1040	* (PO), (CO), (CN)
1036		* (PO), (CO), (CN)
-	932	ω ($C-NH_2$)
899	-	* ν_s CC
877	-	* (C-H)
-	850	* ν_s CC
810	-	CH_2
763	-	ω (C-H)
710	710	* (C-H)
668	-	($C-H_2$), (CS)
610	608	* (PO)
-	575	* (PO)
562	-	* (PO)
int. 530	int. 530	* (S-S)

Results on the bacterial viability

The results obtained in studying the evolution of bacterial viability are shown in Fig. 5, where the respective photos of microorganisms are numbered according to the sample.

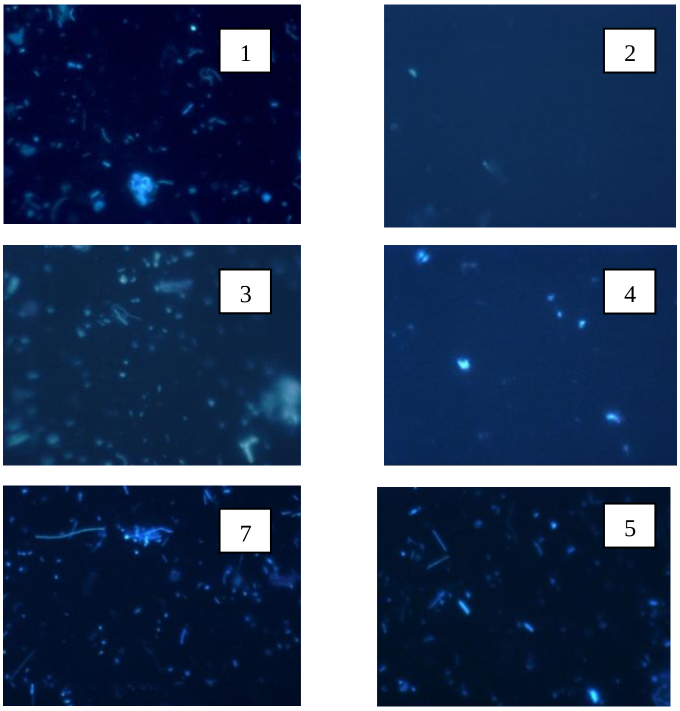

Fig. 5. Photos of microorganisms in samples No. 1-5 and 7.

The highest bacteria count was observed in the containers of samples No. 1, No.3 and No.5, with percentage remaining about the same after adding a polymer. Thus, the daily covering material added to these samples does not affect the viability of biogas-producing bacteria. In the containers with samples No.7 and No.4 respectively 60% and 20% of the micro-organisms remained as compared with this count before adding. For sample No.2 this percent was only 5%, while in the sample No.6 containers no bacteria survived, which means that in these cases the added material has a well-defined negative impact on the viability of bacteria.

4. CONCLUSIONS

1. Analysis of nine commercial samples of different composition has revealed that in the material consisting of straw as a filler and polymer the elements: C, O, Ca, Si, and K are present in all their forms, while Mg, Al, Na, P, Cl, Ti, Zn, Cl, and Br – only selectively.

2. In samples No.1, No.3, and No.4 (with straw as filler) significant amount of Fe was found.

3. In the study it was revealed that the added polymer in sample No.8 (with organic glue as filler) is probably based on polyacrylamide.

4. The viability of biogas-producing bacteria in samples No.1, No.3 and No.5 was found to be the highest (i.e. the highest number of micro-organisms were observed); in sample No.2, No. 4 and No. 7 this viability was significantly suppressed, while in sample No.6 – completely suppressed.

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BIOŠŪNU IKDIENAS PĀRKLĀJUMU IZPĒTE

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K o p s a v i l k u m s

Bioreaktoru pielietošana atkritumu uzglabāšanas sfērā, sakarā ar Direktīvas 1999/31/EC pieņemšanu, ir zaudējusi savu aktualitāti, taču šī metode vēl joprojām var tikt izmantota bioatkritumu noārdīšanai un biogāzes ražošanai. Viena no iespējām kā samazināt bioatkritumu izvietošanu ir biošūnu izmantošana bioatkritumu anaerobai pirmsapstrādei pirms to noglabāšanas. Šūnas piepildīšana ikdienā prasa nepieciešamību izolēt lielāko tās daļu, lai samazinātu gāzes emisiju, smakas, utt. Materiāli, kas ikdienā tiek izmantoti atkritumu pārklāšanai, nepietiekami ietekmē bioprocesus, kas pamatā ir galvenais biošūnas izmantošanas mērķis. Šajā sakarā ir veikta dažādu tirdzniecībā pieejamu pārklājuma materiālu izpēte, pielietojot virkni fizikālo, ķīmisko un bioloģisko metožu, un nosakot svarīgākos parametrus, kas ir būtiski šo materiālu izmantošanai ikdienā kā biošūnas pārklājumu. Pētījumu rezultātā noteikts, ka visatbilstošākie ir materiāli ar bioloģisko izcelsmi, sastāvoši no mazām bio daļiņām ar lielu laukumu bez anaerobo procesu inhibitoriem, piemēram, sēra komponentēm.

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