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STUDYING THE ORGANIC MATTER TRANSFORMATION PROCESSES IN THE COURSE OF COMPOSTING USING HOT-WATER EXTRACTS

Theses of doctoral dissertation

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I. INTRODUCTION

Composting is one of the oldest recycling techniques of mankind, which became neglected after the development of chemical industry. For the more and more urbanised consumers' society it is an increasing technical and environmental challenge what to do with the waste. The number of environmental problems is increasing because the developed industrial society has more and more adverse impacts on environment. The economic aims of 'sustainable' development are the intensive protection of natural resources and obtaining the circulation of the material and energy inputs in the most optimal way. Presently the legislations in the European Union and in Hungary require that the biologically degradable part of waste to be deposited should be decreased. The most common recycling technique of biological wastes is composting.

To study the transformation processes of organic matter in the course of composting is important for the following reasons:

- the transformation of organic matter influences the transformation of other nutrients (e.g. nitrogen transformation processes) to a great extent in the course of composting;
- the transformation of organic matter determines the stability of composts;
- the quality of organic matter influences the effect of compost to the physical, chemical and microbiological properties of soil.

II. OBJECTIVES

In the course of compiling the present Ph.D. dissertation the following objectives were determined:

- Ensuring suitable conditions for composting in small-capacity adiabatic composting reactor, observing the important changes and proving the suitability of the reactor.
- Examining the application of hot-water extraction with the help of samples taken at various stages of the experiment.
- Comparing the method of hot-water extraction and cold-water extraction.
- Determining the ability of easily soluble carbon extraction by calculating the carbon content of hot-water extracts.
- Determining the organic matter content and characterising the more important changes in quality in the course of composting with absorbance examinations of hot-water extracts at UV light.

III. MATERIALS AND METHODS

Horse manure and grape stillage were used in the course of composting.

Table 1.: The properties of raw materials used for composting

Sample	Dry matter %	Loss during heating %	pH (KCl)	Total-N mgkg^{-1}	NH_4-N mgkg^{-1}	NO_3-N Mgkg^{-1}	C/N ratio	Volume weight g/1000 cm^3
Horse manure	57,3	83,5	7,15	8800	649,1	55,9	54,70	650
Stillage	41,2	93,3	6,96	20064	720,9	22,2	26,97	780

The absorbance figures and carbon content of finished composts were compared with data from composts that were aftermatured for half year after finishing composting. The compared composts were the following:

Table 2.: Matured composts used for comparison

Abbreviation	Name	C/N ratio	Organic matter content
CA	Compost of animal origin	8.7:1	22.05
CP	Compost of plant origin	14.7:1	32.49
MC	Mature compost	12.4:1	37.89

Methods

The volume of the adiabatic reactor used for composting was 50 litres. The walls of the reactor were covered by insulating material and the effectivity of the insulation was proved with preliminary testing.

The temperature was measured with a thermocouple (thermoelement) thermometer made of platinum-iridium alloy supplied with permanent electronic data recorder. Composting was completed within 8 weeks (54 days), until the compost temperature was the same as the ambient temperature. Sampling was carried out seven times in the course of composting.

Table 3.: Sampling in the course of composting

Sign of the sample		Time of sampling (day)
Horse manure	Stillage	
HM/1	S/1	0
HM/2	S/2	2
HM/3	S/3	4
HM/5	S/5	8
HM/6	S/6	10
HM/8	S/8	24
HM/10	S/10	54

The hot water extracts from composts were prepared with equipment made by FÜLEKY et al. and patented under number 205994 with the name as „Process for determining the nutrient content of soils, and equipment for its practical implementation”. The pressure of hot water used for extraction was between 100 and 150 kPa, this equilibrium steam tension equals to water temperature of 103 and 105 ^{o}C. 7x100cm^3 extracts were prepared from each sample, the time required for extraction was recorded. During the preparation of cold-water extracts 5 g dry compost was shaken with 100 cm^3 distilled water for 30 minutes, then spinned on a revolution of 10000 min^{-1} for 10 minutes and the liquid was filtered on a filter of 0,45µm.

During the examination of samples the following analytical methods were used:

- Before the analytical examinations the moisture content of the air-dry samples was determined in an exsiccator, drying the samples to body-balance at 105°C.

- The total organic matter content was calculated from the loss occurred during heating. (at 700°C for 5 hours).
- Ph was measured with direct potentiometric method. After calibration, suspensions prepared from 2 g sample and 1M 12.5 cm^3 KCl and H_2O were used. The ph of compost extracts was measured directly.
- The organic carbon content was calculated using the equation of total organic matter (dry matter) / 1,725 and dividing it by the total nitrogen content we get the C/N ratio.
- The total nitrogen content was determined after digestion of samples with sulphuric acid using Parnass-Wagner steam distillation apparatus.
- The carbon content of the extracts was determined by oxidation with chromium sulphuric acid (Tyurin method).
- In the course of UV absorbance examinations, 1:100 dilutions were prepared from the extracts and were measured using BECK DU-50 photometer at wavelength of 254, 410, 465 and 655 nm. The E4/E6 ratio was calculated from the absorbance figures measured at the wavelength of 465 and 655 nm.
- The humus stability coefficient of composts was measured with Hargitai (1988) method. The compost extracts made with NaOH and NaF solutions were measured at three wavelengths (465 nm, 533 nm and 665 nm). From the absorbance figures I calculated the Q value ($Q= E_{NaF}/E_{NaOH}$), then the K value (K=Q/H) using the humus content.

IV. RESULTS

At the beginning of composting the temperature was rising continuously for both materials. In the case of horse manure the termophilic period began on the 3rd day, in the case of stillage even on the 2nd day. In the case of horse manure the observed slower rate of increase was due to the higher C/N ratio (C/N=54,7:1) than the optimal one (C/N=35:1). In the case of stillage the temperature maximum was observed on the 5th day (63,5 ^{o}C). The temperature of both composts reached 55 ^{o}C which is needed for hygienisation.

The ph rose in the first stage of composting. The ph of horse manure increased considerably, however in the last stage it began to decline, but still it exceeded the initial value. The final ph of horse manure was in the slightly basic range.

In the course of composting the carbon content of compost was decreasing. A function was fitted to the data after which the rate constants of the decline in carbon content can be determined.

The rate constant of carbon content for horse manure is 1841 $mgkg^{-1}day^{-1}$ and for stillage 707.58 $mgkg^{-1}day^{-1}$.

Table 4.: The C/N ratio at the beginning and at the end of composting

Time (day)	**Horse manure**	**Stillage**
	C/N ratio	
0	54.76	26.97
54	42.43	17.57
f **$C/N_{0.day}/C/N_{54.\,day}$**	0.77	0.65

In the course of composting the C/N ratio was declining mainly due to the reduction in the carbon content.

During hot-water extraction the time needed for the extraction of the fractions was increasing with the increasing number of fractions in direct proportion.

The ph of extracts differed from that of the KCL-compost suspensions, and the same applies to the fractions extracted in succession from certain samples. In the case of horse manure the ph of extracts, except some fractions (fraction HM/3 1.;and HM/8 5,6,7), is higher (considerably higher in the case of HM/2) than the ph of composts measured in KCl suspension. Both composts (S and HM) have lower ph in water suspension than the fractions do. The ph is increasing in the case of fraction made from HM/1, HM/2, HM/3, HM/5 samples and decreases in the case of HM/6, HM/8, HM/10 samples.

After examining the extracts from horse manure it can be concluded that the most carbon can be extracted from the first fractions for all samples. For samples HM/3 and HM/5 the fractions 2-7 have higher carbon content than the others. In the case of stillage it can also be concluded that always the first fraction has the highest carbon content. After repeating the extraction the consequent fractions have lower concentration of carbon, and there is no considerable difference between the samples. According to the experience with horse manure compost, always bigger

amount of carbon can be extracted from the samples with cold-water extraction. The variation in the carbon content happens parallely in the hot water and cold water extracts.
In the case of stillage, the first three (S/1, S/2, S/3) samples have higher cold-water extractable carbon content than the cumulative carbon content of the seven hot-water fractions. After the fourth sampling (S/5) the carbon content extracted with hot water is higher than the carbon content extracted with cold water.

After finishing the absorbance experiment at UV light, it can be concluded that the highest absorbance was observed in the first fractions for both composts at all four wavelengths.

The absorbance of stillage hot-water extracts at UV light shows a fluctuation; it increases in the first four days, decreasing by the 8^{th} day, then increasing again by the 10^{th} day where it reaches its maximum, and then decreases at all wavelength except at 245 nm, however, the initial value is always higher than the one at the beginning of composting. In the case of horse manure this fluctuation was also noted at the beginning of composting, then the absorbance value started to decline sharply from the 10^{th} day. We could measure absorbance at 665 nm only in the first fraction of HM/10 sample.
When analysing the horse manure extracts, it was concluded that the value of E4/E6 ratio differs only slightly in the first and seventh fraction (except HM/2, and HM/8), it varies between 5 and 8. The measured E4/E6 ratio is lower in the seventh fraction of HM/2 sample than that of the first fraction. The seventh fraction of HM/8 sample showed a higher value than in the first fraction. The absorbance at 665 nm was unmeasurable in the case of 2-7 fractions of HM/10, therefore it was not possible to calculate the E4/E6 ratio.
In the case of stillage compost samples, the E4/E6 ratio is increasing with the increasing number of fractions. The value is between 4.5 and 5.5 in the first fractions and between 6.5 and 7.5 in the seventh fractions. The value of E4/E6 ratio was considerably increasing in the first two days of composting, it was decreasing by the 8^{th} day, then it started to increase again slowly. At the end of composting I could calculate E4/E6 ratio only from the first fraction, which was slightly higher than that of the first fraction of the sample taken at the beginning of composting. It was concluded, that in the case of stillage composting there was no considerable difference between the initial and final figures of E4/E6 ratio. In the first stage of composting (termophilic phase) the value of E4/E6 ratio decreased considerably, then it started again to increase gradually. Similarly

to the horse manure the E4/E6 ratio of the first fraction is slightly lower at the end of composting than the initial value.

During composting the stability index stayed very low for both samples. In both cases the initial increase was followed by a decline. In the case of horse manure the final value slightly exceeds the initial one, as far as stillage is concerned there was a sharp increase observed in the stability index of raw materials and composts.

V. CONCLUSIONS, EVALUATING THE RESULTS

During composting the compost temperature became the same as the ambient temperature by the 26th day for stillage and by 44th day for horse manure. Therefore it is concluded, that the intensive phase of composting completed within 54 days. In the case of horse manure the longer composting period and lower temperature maximum was due to the initial high C/N ratio.

During composting the ph of composts was increasing in the termophilic phase, then it was gradually decreasing with the maturation of composts. The initial increment in ph was the result of ammonification. In the case of horse manure the higher rate of ph increase is explained with the high lingo-cellulose content and the urea.

In the intensive stage of composting the relation between the decrease in the organic carbon content and the time of composting can be described with a linear function, and the rate constant of the decrease in carbon content can be determined. The maturation factor was calculated as the quotient of initial and final C/N ratio, which had a value of 0.77 for horse manure and of 0.65 for stillage. The maturation factor is in line with the results of other experiments. Based on the evaluation of important parameters describing composting process, it is proved that the small-capacity adiabatic composting reactor is suitable for composting different substrates.

During hot water extraction, the time needed for the extraction of each fraction is increasing with the number of fractions. There is a close correlation between the extraction time and the number of fractions (r^2= 0.75-0.95). The water permeability of composts is decreasing with the number of hot water extractions (number of fractions).

The ph of first fractions of compost samples are always lower than that of the further ones because considerable amount of organic matter is dissolved from composts. In the further fractions the amount of organic matter decreases considerably, but supposedly the inorganic ion concentration increases causing basic ph. With the maturation of composts the difference in the ph of hot-water extracts and samples decreases.

The cold-water extracts have higher carbon content than the hot water extracts. In the first stage of composting the easily soluble carbon content is high, therefore in the case of cold-water extracts more easily soluble carbon can be extracted with higher solvent/sample ratio and longer extraction time (30 minutes).

In the case of hot water extraction, the first fractions have higher carbon content than the others. In the case of horse manure on the average 58.08 % of the total extractable carbon (during the 7 fractions) can be extracted with the first fraction, and this value is 67.09 % for stillage. The carbon content of HM/3 and HM/5 samples is higher in 2-7 fractions than in the case of other samples. These samples were taken in the middle (HM/3) and at the end (HM/5) of thermophilic phase, when cellulose molecules were breaking up intensively. The high carbon content of the fraction implies that organic compounds are dissolved from the lingo-cellulose matrix during hot water extraction of lingo-cellulose base composts. From the results of measurements it was concluded that hot water dissolves well the easily soluble organic matter of the samples.

Looking at the results of absorbance experiments, there is a close correlation between the carbon content of the fractions and their absorbance values.

Table 5.: The correlation between carbon content and absorbance

Horse manure		**Stillage**	
Wavelength	**R^2**	**Wavelength**	**R^2**
254 nm	0.9367	254 nm	0.9409
410 nm	0.9797	410 nm	0.8895
465 nm	0.9801	465 nm	0.8966
665 nm	0.9061	665 nm	0.8677

It can be concluded, that after correct calibration, absorbance experiments carried out at any wavelength are suitable for estimating the carbon content of hot-water extracts.

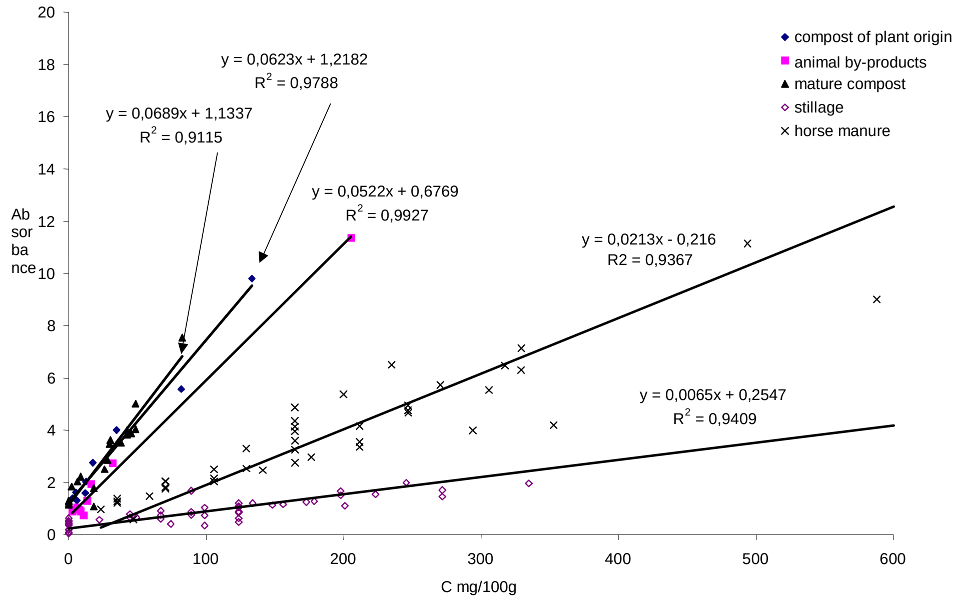

Figure 1.:The absorbance values of composts measured at 254 nm and their correlation with the carbon content

The results measured at 254 nm were compared with similar results of the reference composts. The steepness of the linear function describing the correlation between absorbance and carbon content was examined for different composts. It was concluded that the steepness of the function is increasing with the degree of compost maturation.

Looking at the E4/E6 ratios calculated from absorbance figures, the highest value was observed in the case of fractions 6-7. The amount of organic matter with low molecular weight is increasing with the increasing value of E4/E6 ratio. These data confirm the fact that the increasing number of hot-water extractions pulls away compounds with low molecular weight from the organic matter. The extent of it cannot be determined with the applied methods. The E4/E6 ratio reaches its minimum in all cases of S/2 and HM/5 samples. During composting certain degree of cyclicality was observed. The organic carbon goes through cycles of continuos decomposition and formation in the course of composting. Considerable amount of easily soluble organic compounds (carbohydrates, amino acids, polypeptides, etc.) liberated from the organic matter is built in the microbe population, then with the advance of composting other microbe populations take over due to the changing environmental conditions, thus the easily soluble organic matter content of the substrate. Comparing the first fraction of samples taken at the beginning and end of the process, it can be concluded that the E4/E6 ratio increased slightly (5.3-5.77) in the case of horse manure, while the value decreased (5.5-4.27) in the case of stillage. However it has to be taken into account, that in the practice of soil science the E4/E6 ratios are calculated from $NaHCO_3$ solution extracts and not from water solutions. However, it can be concluded that in the course of composting the rate of fulvic acids with low molecular weight is decreasing in the hot-water extracts.

Studying the Hargitai humus stability coefficients, it can be concluded that in the case of stillage the value was increasing substantially, as stillage has a high sugar and pectin content that are highly biodegradable, and are stabilised in the course of composting. According to the order of magnitude of the stability coefficient both composts are part of the group of raw organic matter. However, it has to be noted that the humus stability coefficients were developed for soils, where the humus substances of composts are more resemble to underwater humus formations.

VI. NEW SCIENTIFIC RESULTS

1.) Studying composts, in the case of applying hot-water extraction the time needed for preparing the same numbers of extracts is increasing with the number of fractions. The water permeability of composts is decreasing with the number of extractions.
2.) By using hot-water extraction the easily soluble carbon content can be extracted effectively in a short time. Most of the hot-water extractable carbon can be found in the first fraction. The hot-water extraction is a suitable method of easily soluble organic matter extraction in the course of composting.
3.) There is a close correlation between the carbon content of extracts and the absorbance figures carried out at various wavelengths (254, 410, 465, 665 nm) in hot-water extracts. After correct calibration, the absorbance experiments at UV range are suitable for measuring the carbon content of hot water extracts.
4.) Studying the measurements done at UV light with hot-water compost extracts, the changes in organic matter can be monitored in the course of composting.
5.) The humus stability coefficient used for describing the stability of humus content in the soil is not suitable for monitoring the changes in quality in the course of composting.

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