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QUANTITATIVE DETERMINATION OF MINERAL PHASES BY THE X-RAY POWDER DIFFRACTION METHOD IN ORGANO-MINERAL SUBSTRATES (DIGESTATE, COMPOST AND ASH FROM BIOMASS)

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Abstract

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In the field of energetics and renewable energy sources, fertilizers, remediation and recultivation, waste management and other, biomass is widely studied and used these days. Determining the mineral phases present in the biomass is essential for determining the binding of chemical elements from which further derives its availability or unavailability for soil processes, plant nutrition or behaviour in technological processes. Semiquantitative phase analyses were carried out by the X-ray powder diffraction method (XRD).

Keywords: X-ray diffraction analysis, Rietveld method, organomineral matrix, compost, digestate, compost mineral, digestate mineral

INTRODUCTION

The question of biomass gets in the society's forefront of interest. In the field of energetics and renewable energy sources, fertilizers, remediation, reclamation and waste management, biomass is widely studied and used. Most of the works are devoted to the research of the organic part of this matrix. However, all the substrates that can be included under the term of biomass also contain variable content of inorganic substances – minerals. Detection of present mineral phases is essential for determining the binding of the element from which further derives its availability or unavailability for soil processes, plant nutrition and behaviour in technological processes. Mineral phases can be defined by the X-ray powder diffraction method. In the case of analysis of the matrix with high proportion of amorphous components – the organo-mineral substrates, it is necessary to use an internal standard. Quantitative content of mineral phases is solved by the addition of an internal standard and using the calculation by the Rietveld method. In this study the mineral phases were determined in compost from two industrial composting facilities, in digestate from three technological processes of the biogas production and in ash originated by burning biomass.

A. Compost

After many decades the management of biodegradable waste is a major theme of modern society again. Biodegradable material is often landfilled without stabilization. Natural and technologically simple way of getting humus from biodegradable waste is composting. Composting is a very old technology applied in small scale productions. Via composts it is possible to stabilize nutrients and organic substances and conveniently put them back to the natural cycle as organic fertilizers hnojivo (Váňa *et al.*, 2004). In the last decade, the number of industrial composting facilities is increasing in the Czech Republic. Raw materials for industrial composting facilities represent 1) greenery waste, 2) biowaste from households, 3) paper waste and 4) specific waste. Biowaste from households obtained as the culled product of municipal waste was often excessively contaminated by extraneous substances (especially heavy metals) from other components of the household waste. The quality of the compost is assessed in terms of the standard CSN 46 5735 for industrial compost; usually the content of essential nutrients (P, K, Ca, Mg and S) and humus substances is determined. These standard prescribed parameters are important in practice, but they do not provide substantial information about the qualitative and quantitative representation of newly formed humus particles (Kolář, Kužel, 2000). None of the usual approaches to the issue of composting evaluates the newly formed compounds, in which the elements occur, or the presence of indigenous or newly formed minerals and their impact on the quality of the compost.

B. Digestate

Digestate is a product of anaerobic decomposition taking place in biogas plants. The primary product of anaerobic decomposition of biodegradable materials is biogas. The secondary output product is the fermentation residue, called digestate. The fermentation residue is applied to land as fertilizer. It can be used as input material in composting facilities, reclamation material or after drying as fuel. The fermentation residue contains high concentration of total nitrogen, out of which 60 to 80% is ammoniacal nitrogen, phosphorus and potassium, which increases the positive influence of digestate when applied to agricultural land (Tambone *et al.*, 2009). The pH of the fermentation residue is usually 7.5 to 8.3 (Gómez *et al.*, 2007). The chemical and mineral composition of fermentation residues is affected by the type of raw materials processed, the manner of pretreatment, technological conditions (operating temperature in the digester, residence time, solids content, etc.) and the manner and time of storage. Liquid fermentation residue usually contains 5 to 12% of total solids, non-liquid fermentation residue 33 to 40% of total solids.

Detailed composition of biogas and fermentation residues, especially from the perspective of minor components which can be considered harmful, is significantly influenced by the kind of input material. Waste from households and industry, which may include cleaning products, pesticides, pharmaceuticals, plastics, synthetic fabrics, paints, etc., very negatively influences the concentration of hazardous compounds in biogas. On the contrary, biogas made from the specifically produced agricultural crops contains the lowest amount of potentially hazardous compounds. The organic materials decomposition value during anaerobic fermentation is between 12 and 53% (Marcato *et al.*, 2008; Menardo *et al.*, 2001). The presence of trace elements and heavy metals in turn could legally prevent the use of fermentation residue as fertilizer on agricultural land. This is particularly the case when materials with high concentrations of these elements are processed in biogas plants, or of biogas plants that use special mixtures of trace elements. Then the content of trace elements and heavy metals in comparison with mineral fertilizers may be higher (Pfundtner, 2002).

C. Ash

Ash is produced by burning biomass in an oxidizing environment. The pilot analyses of ash have been taken as the energy use of composts and digestate is being increasingly considered. Ash is produced by burning biomass in ordinary furnaces and in controlled industrial boilers.

RESEARCH METHODOLOGY

Mineral phases of industrial composts (A) were studied on samples taken at two industrial composting facilities in Brno agglomeration. Samples were taken in June and September 2013. Altogether six samples were taken (two and two raw compost, two compost mixed with soil).

Mineral composition of the fermentation residues (B) was studied on real samples taken from seven agricultural biogas plants in 2013 (five times liquid fermentation, twice dry fermentation). At least two samples were taken from each biogas plant at different times. At the same time, studies have been carried out on four samples from the university laboratory fermenters with a capacity of 120 l. Fermentation residue came from liquid manure, corn and sorghum silage, hay silage and gastro waste. Processes in biogas plants were not chemically modified.

Mineral phases of ash (C) were studied on six samples of laboratory-prepared ash. The mineral composition of ash was studied on six samples burned in an electric furnace in oxidizing atmosphere at 550 °C. The ash was prepared from various biomass, compost, silage and hay.

After being taken, the samples were dried at 105 °C and subsequently milled by a cutting mill into a fraction under 0.100 mm and homogenized. In all samples the following were determined: solids, total organic carbon (TOC), mineral carbon (TIC), combustibles at 550 °C, heat of combustion and the content of mineral phases by the XRD method. Quantitative phase analyses were carried out by the X-ray powder diffraction method (XRD) on the Bruker D8 Advance diffractometer, radiation COKα/Fe, 40 kV/40 mA, the angular interval 2–80° 2θ, step 0.014° 2θ, 0.75 sec., with position sensitive detector Lynxeye. Homogenized powder compositions of samples with the addition of internal standard were used for the analysis. For the internal standardization the ZnO was used in an amount of about 6 wt. % (0.00X g) added to the sample (eg. Mandile, Hutton, 1995). The semi-quantitative phase analysis was carried out by the Rietveld method (Bish, Post, 1993; Bish, Post, 1989) using the Topas program version 4.2.

Obtained Analytical Data

A. Compost

The content of total organic carbon (TOC) in raw composts ranged from 28.6 to 32.1 wt. %, in compost and soil mixtures from the composting facilities it ranged from 14.1 to 15.3 wt. %. The combustion heat in raw composts ranged from 9.18 to 11.61 MJ.kg^{-1}, in compost and soil mixtures from the composting facilities it ranged from 4.46 to 4.92 MJ.kg^{-1}.

By the semi-quantitative phase analysis using the Rietveld method from 64.2 to 72.9 wt. % of the amorphous phase was found out in raw composts, whereas in the compost and soil mixtures from 54.7 to 57.0 wt. % of the amorphous phase was found out. Mineral phases were by majority represented only by Quartz (raw compost from 14.3 to 18.0 wt. %, compost and soil mixtures from 23.5 to 31.5 wt. %) and Albite (max. 7.7 wt. %) and Weddellite (max. 5.1 wt. %) were found in raw composts by minority fraction. Other mineral phases were below 5% and the content of their shares is listed in Tab. I.

B. Digestate

The major part of all samples was formed by the amorphous phase of the content of 77.5 to 96.9 wt. % (median = 91.8 wt. %, variance = 43.5). The content of total organic carbon (TOC) in the evaluated samples was in the interval from 32.0 to 52.0 wt. %. (median = 41.2, variance = 38.6). The contents of the amorphous phase as determined by the XRD method and the total organic carbon contents reach the correlation coefficient of 0.87 in the data set. This check procedure is used to validate the results of the mineral phase analysis. The combustion heat of the digestate has values from 12.67 to 18.06 MJ.kg^{-1}.

Mineral phases of the allochthonous origin with the majority content are represented only by Quartz (LOD–11.8 wt. %). Other minerals are found only in minority fraction: Albite (LOD–2.9 wt. %), Orthoclase (LOD–2.3 wt. %), Illite-muscovite (LOD–3.60 wt. %). These minerals come from agricultural land. They get into the technological process as the contamination of the substrate. (LOD = limit of detection)

Mineral phase of autochthonous origin is represented by Sylvite, which was detected in three samples in the interval from 1.2 to 4.1 wt. %. This is a newly formed mineral which obtains elements for its genesis in plant mass. The growth of this mineral can occur only after the completion of anaerobic decomposition in fermenters, thus in in-process stores of fermentation residues. Its presence is determined by the chemical and physical conditions occurring at these landfills.

Mineral phases with possible allochthonous and autochthonous origin of minority share are Calcite and Magnesium Calcite (1.0 to 5.7 wt. %) which were detected in all samples, and Opal-CT (1.26 to 12.1 wt. %, median = 4.1 wt. %) determined in five samples. Representation of mineral phases in the digestate of individual technologies is shown in Tab. I.

C. Ash

Mineral phases of ashes were formed by Arcanite, C2S alpha, Calcite, Hydroxylapatite, Kalicinite, Quartz and Sylvite, variably represented from accessoric to majority shares. In accessoric shares Anhydrite and Archerite have occurred. Detailed representation of mineral phases in the ash is shown in Tab. I.

RESULTS AND DISCUSSION

In six samples of industrial composts the contents of mineral phases were determined by the X-ray diffraction phase analysis using the Rietveld method. The major component was always formed by an amorphous phase and Quartz. Other mineral phases were detected in the miner to accessoric amount and were made up of the following minerals: Oligoclase, Muscovite, Albite, Orthoclase, Microcline, Chlorite, Calcite and Amphibole. In the raw composts the minerals Weddellite (LOD–5.1 wt. %) and Whewellite (LOD–4.9 wt. %) were detected.

In raw composts mineral phases with smaller content were identified, but with greater variability. In compost and soil mixtures from the industrial composting facilities less mineral phases were found, but with a higher proportion. These changes are variable, depending on the available composting materials and on soil resources used for making compost. Soil is used according to the currently negotiated contracts with other organizations. Most often the overburden soil is used and it is returned to its place of origin after the incorporation into compost and after completion of the project at the site of origin (construction, remediation).

The identified mineral phases Weddellite and Whewellite are organogenous minerals – calcium oxalates. Oxalates are present in some plants whose remains are used for composting. Oxalic acid may also be produced by decomposition of organic substances. These minerals are formed by primary crystallization, or in some case interchange

I: *Mineral phase in the commercial compost and digestate*

Mineral Phase	Raw compost	Compost and soil mixture	Digestate Liquid Fermentation	Digestate University fermenters	Digestate Non-liquid Fermentation	Ash
	n = 4	n = 2	n = 10	n = 6	n = 4	n = 6
	[wt. %]	[wt. %]	[wt. %]	[wt. %]	[wt. %]	[wt. %]
Amorphous content	64.2–72.9	54.7–57.0	89.2–96.9	78.5–91.3	77.5–90.4	
Quartz	14.3–18.0	23.5–31.5	LOD–5.6	LOD–0.6	7.3–11.8	LOD–12.9
Oligoclase An16	LOD–10.2					
Illit-muscovite	1.3–3.6	LOD–4.4			LOD–3.6	
Albite	1.3–3.6	LOD–7.7	LOD–2.5		2.1–2.9	
Orthoclase	LOD–3.1	2.8–3.7	LOD–0.9		LOD–2.3	
Archerite						LOD–2.88
Kalicinite						LOD–34.1
Microcline	LOD–2.9					
Chlorite	LOD–0.6	1.0–1.6				
Hydroxylapatite						8.5–20.9
Calcite	LOD–0.4	4.9	LOD–5.7		LOD–1.75	LOD–56.6
Anhydrite						LOD–2.8
Arcanite						6.5–22.4
C2S alpha						LOD–19.5
Hornblende	LOD–0.4	0.6–3.6		LOD–0.1		
Opal-CT			LOD–3.0	4.1–12.1		
Weddellite	LOD–5.1					
Whewellite	LOD–4.9					
Sylvite			LOD–1.2	LOD–4.1		7.7–23.4
Total organic carbon (TOC)	28.6–32.1	14.1–15.3	41.2–52.0	34.7–37.4	32.0–42.0	
Combustion Heat [MJ.kg^{-1}]	9.18–11.61	4.46–4.92	15.68–18.06	11.48–15.99	12.67–15.49	
LOD – limit of detection						

each other with ongoing hydration and dehydration. These minerals are biodegradable in soil, providing elements for plant nutrition.

Mineral phase composition was analysed on samples of fermentation residues from seven agricultural biogas plants and a university biogas plant. The content of total organic carbon (TOC) ranged from 32.0 to 52.0 wt. %. (median = 41.2 wt. %). The majority of all samples was formed by the amorphous phase (from 77.5 to 98.7 wt. %, median = 91.8 wt. %). Minority phases consisted of Quartz (0.22 to 11.94 wt. %), Albite (2.15 to 2.92 wt. %), Orthoclase (0.86 to 2.31 wt. %), Muscovite (LOD–3.60 wt. %), Amphibole (LOD–0.12 wt. %). They were detected in all fermentation residues in various proportions depending on the local pedological situation. The largest amount of these admixtures was found in biogas plants with dry fermentation. These minerals are natural in this process; in case of using the fermentation residue as a fertilizer they are returned to the soil. Calcite or Magnesium Calcite (from 1.0 to 5.7 wt. %) were also found in all samples. This mineral has its possible origin in the allochthonous environment or autochthonous reactions. Its presence stabilizes the pH in the fermenters and the pH of the fermentation residue. In five cases Opal-CT was found (1.26 to 12.1 wt. %, median = 4.1 wt. %). Opal-CT may be brought into the fermenters as part of the plant tissue, so called Phytoliths, or admixture of other origin; it may also originate from the present amorphous SiO_2.

CONCLUSION

In six samples of industrial composts, twenty samples of digestate and in six samples of ash the contents of mineral phases were determined by the X-ray diffraction phase analysis using the Rietveld method.

The analysis of the compost mineral phases provides information on the elements links needed for plants nutrition and brings unconventional information on the quality of produced composts and digestates from biogas plants. In the case of ashes the determination of mineral phases allows estimating the behaviour of ashes in technological units and disposal options, or more precisely their further use.

SUMMARY

In the field of energetics and renewable energy sources, fertilizers, remediation and recultivation, waste management and other, biomass is widely studied and used these days. Determining the mineral phases present in the biomass is essential for determining the binding of chemical elements from which further derives its availability or unavailability for soil processes, plant nutrition or behaviour in technological processes. In six samples of industrial composts, twenty samples of digestate and in six samples of ash the contents of mineral phases were determined by the X-ray diffraction phase analysis using the Rietveld method. The analysis of the compost mineral phases provides information on the elements links needed for plants nutrition and brings unconventional information on the quality of produced composts and digestates from biogas plants.

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