Characterization of biochar produced from sewage sludge for the purpose of material recovery

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Abstract: Pyrolysis is a technological process and waste procedure, aiming at recovery of organic matter with energy production potential. Biochar, as a solid residue of pyrolysis, is suitable for recycling the organic matter (TOC) and the inorganic matter, e.g. nutrients (P, K, N), contained in sewage sludge. Biochar from pelletized sewage sludge was prepared in the laboratory using advanced thermogravimetric techniques (TGA/DTG) with varying parameters. Resulting biochar have different qualities and properties, according to preparation condition. The samples were tested to determine the ultimate physico-chemical parameters, which affect biochar applicability. Mineralogical characterization of the resulting biochar has been accomplished by a combination of two advanced analytical techniques: i) XRD and ii) SEM-EDS.

Keywords: pelletized sewage sludge; TGA/DTG; biochar; material recovery.

Introduction

Pyrolysis is a thermochemical decomposition of biomass into a range of useful products. The process is typically carried out in a temperature range from 300 ^{o}C through 650 ^{o}C, Prabir [1]. During pyrolysis, large, complex hydrocarbon molecules of biomass break down into relatively smaller and simpler molecules, forming gaseous and liquid products, and solid residue – the biochar. Pyrolysis offers a potential of material utilization of sewage sludge. The densified organic fraction of sewage sludge is suitable for energy utilization, and on the other hand the yielding solid residue is useful for material utilization on fields or forests. Biochar is by mass the major pyrolytic product. Its characteristics make it promising for application in agriculture due to its high immobilization affinity of heavy metals, Mislej et al [2]. Biochar retains the main part of carbon in stable solid form, Prabir [1]. In addition, biochar contains a higher content of phosphorus, potassium and nitrogen Prabir [1], which further demonstrates the great potential of its use as a fertilizer.

Material and Methods

Biochar was prepared from a representative, mass-proportionally composed annual sample of dried, anaerobically stabilized sewage sludge (further referred to as pellets) produced at wastewater treatment plant with capacity of 360,000 PE, WWTP [3]. Two forms of the sample were tested: i) milled pellets <0.1 mm (Sample A) and ii) granulated dried sewage sludge, d_{90} = from 2 mm to 4 mm, as pellets (Sample B). Sampling of pellets, physico-chemical characterization of pellets and biochar, preparation and determination of leachate, Technical Standard [4], and testing of the water-soluble portion of resulting biochar, Technical Standard [5], were made by standard methods relevant for a particular area of investigation. Determined quality of resulting leachates were evaluated according to demands, presented by Slovenian legislation, [6].

Using the advanced laboratory thermogravimetric analysis (TGA/DTG in the atmosphere of argon, 99.999% by volume), Pfeiffer [7], the pellets were thermally treated under different conditions. Sample A was thermally treated by three different procedures: i) 50 mg of the sample was dynamically heated at 10 $Kmin^{-1}$ in the temperature range from T_{room} to T = 1500 °C (sample A1), ii) 2000 mg of the sample was isothermally heated for 60 minutes at 450 °C (sample A2), iii) 2000 mg of the sample was isothermally treated for 180 minutes at 900 °C (Sample A3). No air or other atmosphere was initially present in any case.

Sample B was isothermally processed in two ways: i) 2000 mg was isothermally heated for 60 minutes at 450 °C (Sample B1) and the same mass of the sample B was isothermally heated for 600 minutes at 450 °C (Sample A4). No air or other atmosphere was initially present in any case.

Mineralogical characterization of the resulting solid residues (biochars) has been accomplished by a combination of two methods: i) morphology, microstructure and semi-quantitative chemical analysis by scanning electron microscopy (SEM) and electronic dispersion spectroscopy (EDS), with the use of the apparatus JEOL 5500 LV, and ii) x-ray diffraction (XRD), which was carried out by X-ray powder diffractometer Empyrean, PANalytical; analysis were conducted at voltage of 45 kV and40 mA current with a Cu Kα anode, in an angular range of 20-70 °(2θ) with 0.02 °(2θ) step and integration time of 200 s.

Results and Discussion

Due to the high carbon content (Table 1), the biochar has relatively high calorific value. Biochar has other advantageous physical properties, such as certain specific surface area. This is greater in biochar produced at a higher temperature (Table 1, 4). We have found that the cadmium compounds, lead and zinc compounds are very volatile at increased temperature and they remain in low concentrations in the biochar (Table 2).

Table 1: A comparison of quality of pellets and the resulting biochars.

Parameter	Unit	Sample A	Sample A2	Sample A3
Temperature of thermal load; pyrolysis	^{o}C	-	450	900
Diameter, d_{90}	mm	< 0.1	< 0.1	< 0.1
Specific surface area, BET	m^2/g	0.94	4.81	15.56
Dry solid content	%	90.6	n. a.	
Ash content at 550 ^{o}C	% d.s.	32.02		
Ash content at 900 ^{o}C	% DS	28.47		
TOC	C, % d.s.	38.4	29.4	30.3
TC	C, % d.s.	40.4	29.4	30.7
Hydrogen	H, % d.s.	4.40		0.83
Nitrogen	N, % d.s.	6.15	4.12	1.53
Phosphorus	P, % d.s.	2.22	n.a.	5.20

Table 2: A comparison of content of heavy metals in pellets and the resulting biochars.

Parameter	Unit	Sample A	Sample A2	Sample A3
Arsenic	As, mg/kg d.s.	3,5	4,7	4,2
Barium	Ba, mg/kg d.s.	320	n.a.	640
Cadmium	Cd, mg/kg d.s.	1,23	2,4	0,1
Chromium, $_{total}$	Cr, mg/kg d.s.	120	230	220
Copper	Cu, mg/kg d.s.	350	680	650
Molybdenum	Mo, mg/kg d.s.	8,3	n.a.	23
Nickel	Ni, mg/kg d.s.	86	170	160
Lead	Pb, mg/kg d.s.	93	180	12
Antimony	Sb, mg/kg d.s.	4,3	n.a.	9
Selenium	Se, mg/kg d.s.	3,4	4,1	4,4
Zinc	Zn, mg/kg d.s.	1000	2200	83

The quality of leachate derived from biochar (Table 3), exhibits that the biochar is a non-hazardous material and could be used for burdening of soil with waste spreading and for the reclamation of soil or as compost additive [6]. The quality of biochar does not differ too much from the requirements for the quality of inert materials (Table 3) - the values for antimony and total dissolved solids are only slightly exceeded.

The proportion of water-soluble phosphorus in biochar, in relation to the total phosphorus (Table 4), does not differ significantly from the share that is soluble in pellets. The proportion of water-soluble potassium in biochar decreases significantly with temperature (Table 4).

The powder diffraction analysis of samples A, A2 and A4 (Figure 1) revealed that their mineralogical composition is fairly similar. The carbonates (calcite, dolomite) and quartz are the major mineral phases. In sample A, the magnesium phosphate (struvite) was detected as a minor phase. The magnesium phosphate was defined further by SEM/EDS in all of the samples, the most and the least abundant in samples A and A4 respectively.

Table 3: Results of derived Leachate test (EN 12457-4, LS=10 l/kg, dry solid) for characterization of biochars.

Parameter	Unit	Limit values for non-hazardous waste	Limit values for inert waste	Sample A2	Sample A3
pH	-	-	-	7.2	12.2
Arsenic	As, mg/kg d.s.	2	0.5	0.051	0.014
Barium	Ba, mg/kg d.s.	100	20	4.8	3.1
Cadmium	Cd, mg/kg d.s.	1	0.04	<0.002	<0.002
Chromium, $_{total}$	Cr, mg/kg d.s.	10	0.5	0.013	0.056
Copper	Cu, mg/kg d.s.	50	2	0.025	0.019
Molybdenum	Mo, mg/kg d.s.	10	0.5	0.35	0.10
Nickel	Ni, mg/kg d.s.	10	0.4	0.0037	0.018
Lead	Pb, mg/kg d.s.	10	0.5	0.0039	<0.002
Antimony	Sb, mg/kg d.s.	0.7	0.06	**0.10**	**0.063**
Selenium	Se, mg/kg d.s.	0.5	0.1	0.018	0.049
Zinc	Zn, mg/kg d.s.	50	4	**7.3**	3.9
DOC	C, mg/kg d.s.	800	500	349	275
Total disolved solids	mg/kg d.s.	60.000	4.000	**7,420**	n.a

Table 4: A comparison of the nutrient content in pellets and in biochars.

Parameter	Fraction	Unit	Sample A	Sample B1
Specific surface area; BET	Solid	m^2/g	0.9433	6.82
Bulk density		$kgdm^{-3}$	0.82	0.82
P		% d.s.	2.22	4.09
N			6.15	4.12
NH_4-N			1.0	n.a.
Mg			0.965	1.90
K			0.30	0.41
pH	Water soluble nutrients (EN-13652; 1+5)	-	7.8	8.0
P		% d.s. of P_{total} mg/kg $_{DS}$	5.76 1,282	5.37 2,195
NH4-N		% d.s. % d.s. of N_{total}	1.03 21.5	n.a.
Mg		% d.s. of Mg_{total} mg/kg $_{d.s.}$	1.91 184	1.3 246
K		% d.s. of K_{total} mg/kg $_{d.s.}$	23.6 706	3.82 156

According to the results of the SEM/EDS analysis, the minor phases are also grains of calcium phosphate and amorphous grains composed of Si, Al, K and Ca/Fe (Figure 3).

In samples A2 and A4, particles of graphite can be found. The samples A3 and A4 are different from A and A2. In the Figure 2, the xrd patterns of the samples are presented.

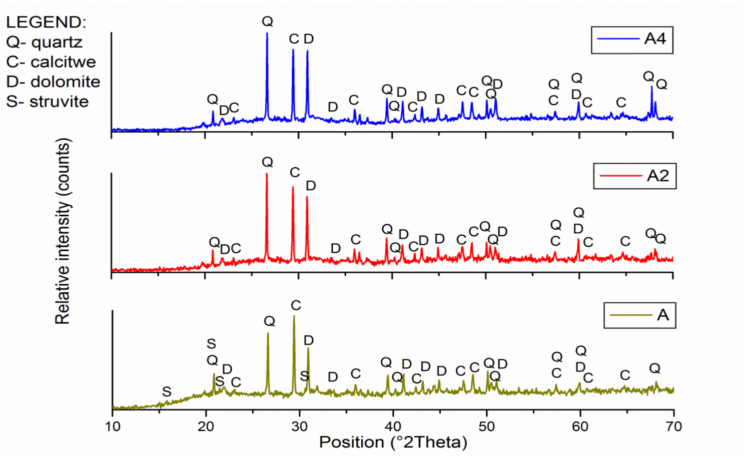

Figure 1: XRD patterns of samples A, A2 and A4.

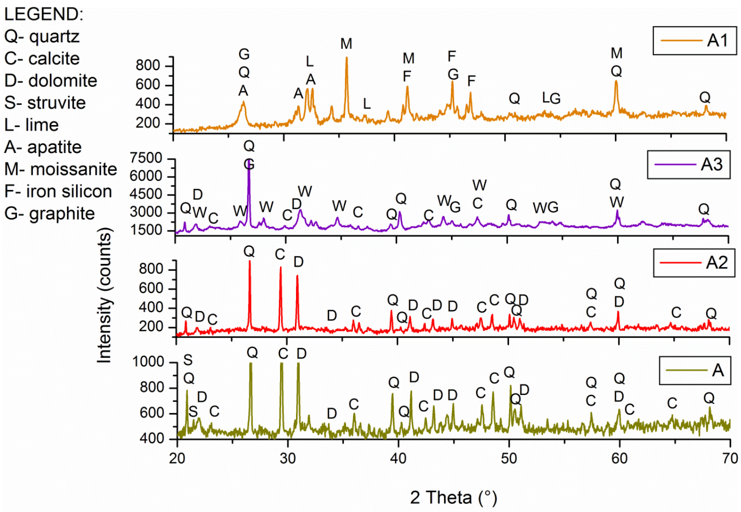

Figure 2. XRD patterns of samples A, A2, A3 and A1.

As a consequence of the higher temperature, the quantities of carbonates (calcite, dolomite) are very low in the sample A3, while in the sample A1 they were not identified. Calcium (magnesium) phosphate is present in the sample A3.

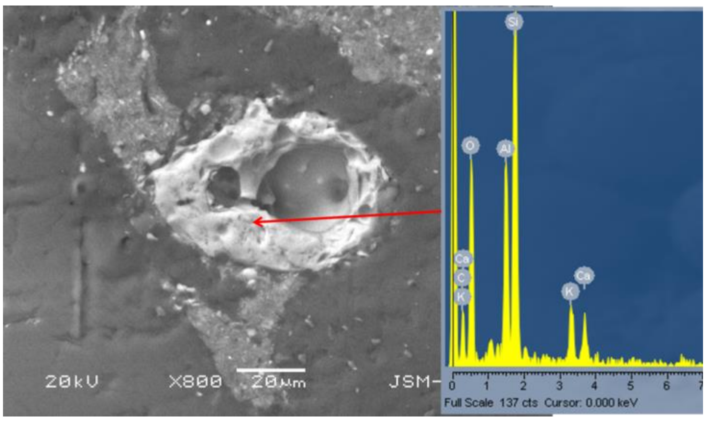

Figure 3. Micrograph of the amorphous grain in the sample A2, with the EDS analysis.

The phase composition of the sample A1 shows that silicon carbide, apatite and lime can be present, but detailed further analysis should be performed in order to endorse such conclusions. SEM/EDS analysis of the sample A1 revealed the presence of spherules, composed mainly of Ca, Si and Al.

Conclusions

The resulting biochars showed interesting qualities and properties. It provides an alternative to the complete burning of sewage sludge, which releases all the carbon in to the atmosphere. Due to the high carbon content (Table 1), the biochar has relatively high calorific value and is therefore interesting for further energy utilization as a solid alternative fuel or for material utilization as a fertilizer. In addition, biochar contains a higher content of phosphorus, potassium and nitrogen, which further demonstrates the great potential of its use as a fertilizer. In addition to nutrients, pellets contain many interesting inert materials, such as silicon, aluminium, iron and calcium compounds.

Because of a relatively high proportion of various materials, it is very important that the final processing of pellets considers: i) the most energy-efficient conversion of organic part, ii) material utilization of nutrients, such as phosphorus, potassium and nitrogen, and iii) a optimum end-use of residual inert inorganic portion.

The pyrolysis of sewage sludge, as a pre-processing procedure, allows useful utilization of the major substances in the sewage sludge - an energy utilization of the densified organic fraction and material recovery of the resulting biochar.

Literature

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