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STABILITY PROPERTIES OF BIOSLUDGE-WOOD ASH COMPOSITES

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ABSTRACT

Mixtures of secondary biosludge from 100 % recycled paper production and deinking as well as wood ash were prepared in different proportions and subsequently analyzed fresh and after ageing in anaerobic conditions for their chemical and biostability properties. Dry matter and ash contents were determined and water leachates prepared. Conductivities, pH and redox potentials were measured in water extracts as well as concentrations of different ions, heavy metals and organic acids. The results indicated that appropriately prepared mixtures are chemically and biologically enough stable to be used as secondary raw materials for landfill covering.

Key words: secondary biosludge, deinking ash, wood ash, chemical properties, biostability.

INTRODUCTION

Waste paper sludge is typically generated on effluent treatment instalations in paper mills. Due to strict legislation only chemimechanical water cleaning is usually not enough to eliminate water soluble lower molar mass contaminants and reduce COD, so more and more biological effluent cleaning has been introduced. Consequently large quantities of biosludge are being produced on biological water treatment plants Microorganisms in the secondary water treatment process use the organics in the water as food. Biosludges are primarily composed of microbial biomass, with minor portions of other inorganic and organic solids. They typically contain low solids content as they are composed of biological cells which are difficult to dewater. Biological sludges represent waste material unless they are reprocessed and in somewhat modified form or mixed with other waste solids used for practical purposes. It has been established by preliminary experiments that wood and deinking sludge ashes can be efficiently utilized as additives to biosludge. Wood ashes are being produced by incineration of different sorts of waste biomass. Deinking sludge is produced in the process of removing printing inks from the paper during paper recycling and is usually incinerated together with wood residues. Ashes represent waste, however the fact is that the moisture content of biosludge is greatly reduced when it is mixed with ash and at the same time it becomes much more stable against microbial deterioration due to alkaline pH values which inhibit biological activity. If both materials are mixed in optimal proportions new geotechnical products are produced which may find their use in construction business, for example they may be used for landfill covering. However the newly prepared materials should be first tested for their physico-chemical and biostability as well as geotechnical properties (1-10).

The aim of the research was to establish whether appropriately prepared biosolids were chemically and biologically sufficiently stable to be used for landfill covering.

EXPERIMENTAL

Samples

Secondary biosludge from biological water treatment plant was obtained from a paper mill producing 100 % recycled paper.
Mixed ash was obtained by incineration of wood waste and deinking sludge while wood ash originated from incineration of wood residues.

Sample preparation and ageing

Homogenized mixtures of mixed ash and biosludge were prepared in proportions 60:40 and 70:30 while corresponding mixtures of wood ash and biosludge were prepared in proportion 70:30 only. They were filled into cylindrical vessels (50 l) and covered with a compact layer of earth by which typical landfill conditions were simulated. Mixtures were aged for 12 and 9 months respectively. Samples of the materials were taken for chemical tests at different time intervals from the bottom.

Table 1.: Dry matter and ash contents of fresh and aged mixed ash/biosludge composites.

Sample	**Dry matter %**	**Ash (550 ºC) %**	**Ash (900 ºC) %**
60 : 40 initial value	65,6	92,0	84,4
60 : 40 3 months	71,2	92,5	84,5
60 : 40 5 months	71,4	93,3	84,7
60 : 40 7 months	71,7	93,2	84,8
60 : 40 8 months	71,9	93,4	84,8
60 : 40 12 months	72,1	93,6	84,8

Analyses

Dry matter and ash contents (500 and 900 ºC) were determined according to prescribed standard methods. Water extracts were prepared according to the DIN 38414-S4 standard. They were subsequently analysed for pH, redox potential, conductivity, TOC (total organic carbon), concentrations of various ions NH_4^+, Cl^-, SO_4^{2-}, PO_4^{3-}, NO_3^-, CO_3^{2-} and volatile organic acids (formic, acetic, propionic, butyric, glycolic and lactic). All ions and acids were determined by ion chromatography. Heavy metals were determined by AAS (atomic absorption spectrometry). Results are average values of 3 individual measurements.

Results and discussion

Dry matter of fresh biosludge was typically between 15 and 20 % which is very low. After mixing with ash the corresponding values substantially increased. They also somewhat increased with ageing time. Ash contents of mixtures were very high as expected. The results are collected in tables 1, 2 and 3.

Table 2.: Dry matter and ash contents of fresh and aged mixed ash/biosludge composites.

Sample	**Dry matter %**	**Ash (550 ºC) %**	**Ash (900 ºC) %**
70 : 30 initial value	73,5	90,5	82,6
70 : 30 3 months	83,1	91,5	86,2
70 : 30 5 months	82,1	91,8	85,8
70 : 30 7 months	82,4	92,7	85,0
70 : 30 8 months	82,7	92,4	85,2
70 : 30 12 months	82,7	92,7	85,3

Table 3.: Dry matter and ash contents of fresh and aged wood ash/biosludge composites.

***Sample**	**Dry matter %**	**Ash (550 ºC) %**	**Ash (900 ºC) %**
70 : 30 initial value	50,9	86,8	77,5
70 : 30 2 months	52,4	87,3	77,5
70 : 30 3 months	54,2	87,4	77,7
70 : 30 9 months	58,1	88,1	77,9

* experiment started 3 months later as in the first 2 cases and biosludge had slightly different characteristics (dry matter content)

The water leachates of fresh biosludge had pH values between 8,1 and 8,3. They emitted specific unpleasant odour. After mixing with ash the corresponding pH values increased to about 12 and remained stable with ageing time while the smell disappeared. Redox potentials were negative thus indicating oxygen consumption within the materials.

Conductivities did not change significantly throughout the experiment. The results are collected in tables 4, 5 and 6.

Table 4.: pH, redox potential and conductivity values of water extracts of fresh and aged mixed ash/biosludge composites.

Sample	pH	Redox potential mV	Conductivity µS/cm
60 : 40 initial value	12,5	- 65	12800
60 : 40 3 months	12,3	- 64	11510
60 : 40 5 months	12,7	- 95	10500
60 : 40 7 months	12,6	- 102	10020
60 : 40 8 months	12,1	- 126	9500
60 : 40 12 months	12,1	- 126	9500

Table 5.: pH, redox potential and conductivity values of water extracts of fresh and aged mixed ash/biosludge composites.

Sample	pH	Redox potential mV	Conductivity µS/cm
70 : 30 initial value	12,5	- 59	10550
70 : 30 3 months	12,3	- 58	10920
70 : 30 5 months	12,7	- 68	10910
70 : 30 7 months	12,7	- 91	10600
70 : 30 8 months	12,1	-94	10150
70 : 30 12 months	12,3	- 22	10500

Table 6.: pH, redox potential and conductivity values of water extracts of fresh and aged wood ash/biosludge composites.

Sample	pH	Redox potential mV	Conductivity µS/cm
70 : 30 initial value	12,0	- 76	12300
70 : 30 2 months	11,8	- 72	15070
70 : 30 3 months	11,6	- 84	14540
70 : 30 9 months	11,7	- 50	12530

The most abundant leachable anions were chloride, sulphate and carbonate whose concentrations varied similarly as conductivities. Concentrations of NH_4^+ and NO_3^- constantly decreased while PO_4^{3-} remained very low and almost constant. The results for NH_4^+, Cl^- and SO_4^{2-} are expressed as mg of ionic species per kg of dry composite. They are collected in tables 7, 8 and 9.

Table 7.: Concentrations of leachable ions in fresh and aged mixed ash/biosludge composites.

Sample	**NH_4^+ mg/kg**	**Cl^- mg/kg**	**SO_4^{2-} mg/kg**
60 : 40 initial value	120	1546	567
60 : 40 3 months	94	1590	568
60 : 40 5 months	80	3900	350
60 : 40 7 months	59	5952	215
60 : 40 8 months	58	3105	100
60 : 40 12 months	50	1700	120

Table 8.: Concentrations of leachable ions in fresh and aged mixed ash/biosludge composites

Sample	**NH_4^+ mg/kg**	**Cl^- mg/kg**	**SO_4^{2-} mg/kg**
70 : 30 initial value	87	1260	432
70 : 30 3 months	48	1110	580
70 : 30 5 months	29	2970	783
70 : 30 7 months	25	3155	566
70 : 30 8 months	12	1665	394
70 : 30 12 months	12	1520	315

Table 9.: Concentrations of leachable ions in fresh and aged wood ash/biosludge composites.

Sample	**NH_4^+ mg/kg**	**Cl^- mg/kg**	**SO_4^{2-} mg/kg**
70 : 30 initial value	21	27310	287

70 : 30 2 months	38	19250	264
70 : 30 3 months	60	19570	190
70 : 30 9 months	55	16255	160

TOC values of water leachates increased with ageing time thus indicating that a portion of organic material initially present became soluble due to decomposition of larger molecules to smaller molecular units. Concentrations of volatile organic acids correspondingly rose during the time of ageing experiment, however the latter did not reach values which could have caused emission of bad smell. As organic acids are typical products of microbial deterioration of organic materials their increasing concentrations indicate that biodegradation is in progress. By the end of the experiment after 12 months the amount of organic matter was reduced by 20 to 23 % which can be calculated from the increase of ash content. TOCs and concentrations of volatile organic acids are presented in figures 1, 2, 3 and 4.

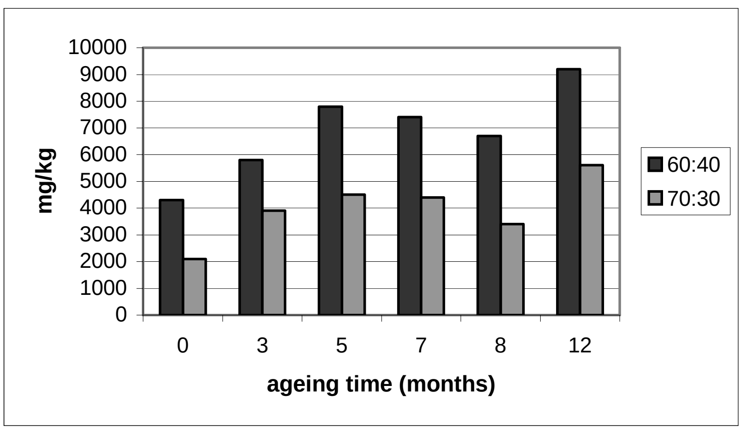

Figure 1.: Leachable TOC in fresh and aged mixed ash/biosludges composites.

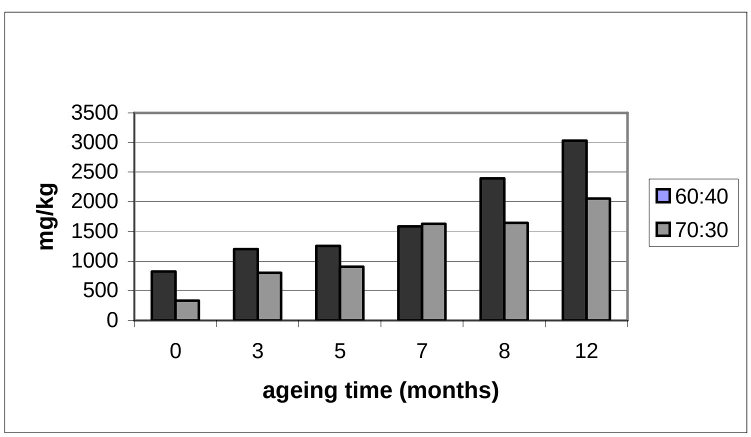

Figure 2.: Volatile organic acids in fresh and aged mixed ash/biosludges composites.

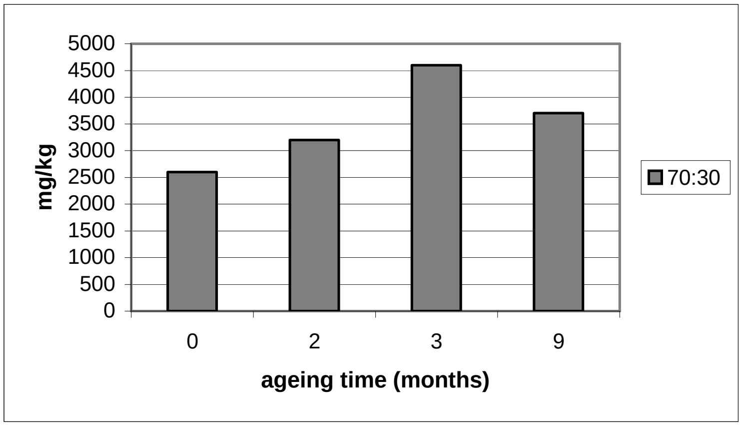

Figure 3.: Leachable TOC in fresh and aged wood ash/biosludges composites

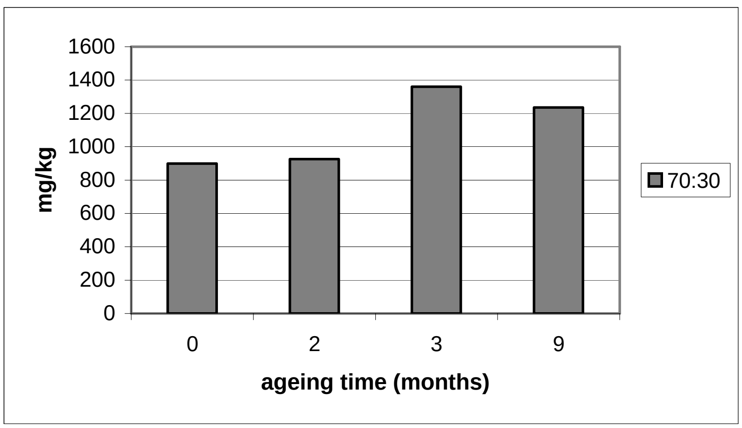

Figure 4.: Volatile organic acids in fresh and aged wood ash/biosludges composites

Concentrations of leached heavy metals at the end of the experiment are collected in table 10 All values are low except those for leachable copper in cases of composites with mixed ash. Most probably majority of copper originated from printing ink residues which constituted deinking ash.

Table 10.: Concentrations of leachable heavy metals in ash/biosludge composites after 12 and 9 months.

Sample	**Cu (mg/kg)**	**Ni (mg/kg)**	**Cd (mg/kg)**	**Pb (mg/kg)**	**Cr (mg/kg)**	**Zn (mg/kg)**
60:40 (mixed ash)	71	3	< 0.01	0.4	0.6	0.4
70:30 (mixed ash)	128	6	< 0.01	0.7	0.8	0.6
70:30 (wood ash)	38	6	< 0.01	1.2	0.6	0.5

By mixing with ash biosludges became more alkaline and resistant against specific biological degradation leading to evolution oh highly toxic H_2S. At high pH values the developed odorous volatile organic acids were also neutralized. Mixture 60:40, containing greater portion of biosludge leached relatively high TOCs (>7500 mg/kg) which is not allowed for landfill applications according to the current legislation. The situation was much better in case of 70:30 mixtures, however 70:30 mixed ash/biosludge composite leached too much copper as the limiting value of 50 mg/kg was exceeded. All the materials were slowly chemically and biologically stabilizing with time.

CONCLUSION

According to chemical and leaching properties mixtures with lower organics content (30 % or even less) seem to be quite suitable fur further application. Tests of their geomechanical properties have shown very promising results from which it can be concluded that newly developed composites could be conveniently applied as secondary raw materials in landfill construction, providing that they are mixed in proper proportions. By transformation of generated industrial waste into useful products serious ecological problems can be solved and more efficient waste management achieved. At the same time new products are obtained which may replace valuable natural raw materials in numerous practical applications.

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