

# Investigation of Biomass Ash Properties for Their Utilization Assesment

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*Abstract.* Ash is a mineral waste group, which quantity increases on a global scale and now it has achieved hundreds of millions of tons, and as they are an integral part of the any solid fuel, including biomass the production rate will continue. At the same time ash, due to their nature and composition is a unique material that can be valuable technogenic resource.

The paper studies the wood ash physical properties (density, porosity, specific free surface) composition and the metal adsorption ability. It was found that wood ash contains a significant percentage of metals in the mobile phase, which dissolve in the water and thus are able to spread into the surrounding soil. The study established a high adsorption activity of ash (95-99%) to the metals. It was found that the adsorption capacity of the ash is possible to increase with the activation of the ash particle surfaces and changing the pore structure.

Keywords - biomass ashes, specific free surface, adsorption capacity, physical properties of ashes.

## I INTRODUCTION

Fuel contains the inorganic mineral components which after fuel combustion form ash. The quantity, composition, structure and properti of ash depend primarily on the fuel type and composition. Gaseous fuels practically does not have ash, fuel oil gives very little ash (depending on the type of fuel, for example, diesel - 0.01%, oil- 0.15-0.3%), soli fuel has the highest ash content fluctuation rang. The highest ash percentage have solid fossil fuels. A coal contain ash ranging from 2 to 50%, lignite -8-48%, oil shale -50-72% [1,2]. Peat, which is located in the buffer zone between fossil fuels and biomass, has ash from even 1% (high peat bogs -2-4%) to 20% (low peat bogs 6-18%)[3,4]. As a result, the world eergy sector as well as all other sectors that use fuels formed large quantity of mineral waste - ash and disposal and managing of this volume is problem which solving has recently become acute. Thus, the Russian Federation is produced Thus, the Russian Federation is produced over 28,10<sup>6</sup>tons of ash per year. Siberian Federal District have collected 300.10<sup>6</sup> tons of unused ash.Statistical data. show that only the fly ash content in the world grows up  $180.10^6$  tons per year [5]. The use of Biomass - (wood, energy plants, straw, reeds) for heat production gives a much lower ash outcomefrom 0.5 to 12% depending on the types of plants and their growth conditions (wood-0,3-1,0%, straw - 4.5 to 11.3%) [6]. Thus, the transition to renewable energy sources - biomass seriously reduces the weight of the ash forming, but not solve the problem as a whole.For example, Finland in energy-use fuel - wood and peat annually produces  $6.10^5$  tons of ash, but in general, the pulp and paper industry and other companies which use wood as fuel, this amount constitutes  $1,02.10^6$  tons of ash per year. The same situation in Sweden -  $8.10^5$  tons of wood ash per year. In the US. annually is produced approximately 3.10<sup>6</sup> tons wood ash, in the China  $-20.10^5$  t per year [7]. In the Latvia putting out timber volume consumed for heat generation and industrial technology and taking into account the average wood ash content around 3% the annual production of ash is not less than 30000 tons. Consequently, the optimal utilization of ash is an essential to the Latvian conditions also, especially in view of the national and the EU's energy development strategy relating to the transition to renewable energy sources, including biomass. It is necessary to note that the solid organic waste for energy production gives the additional increase in the amount of ash. Also, from an environmental point of view and rational exploiting of resources it is important to find the optimal methods to utilize ash as technogenic resource [8].

Their composition, structure and properties are very diverse, and their use is therefore associated with the ash parameter studies[9,10,16,21,29]. Ash utilization problems in the world are widely studied, the technology is put into practice. The main directions of ash application at the moment may be divided into 4 groups : agriculture, construction and building, production of materials, water purifying. These directions are summarized in the table below (Table 1).

Agriculture[7,24,25,26]	Construction[12,15,17,20,23]	Material production[11,12,13,14,15]	Water treatment[18,19,32]
<ol> <li>1.Mineral fertilizers for soil improvement</li> <li>2.Composting component</li> <li>3.Litter</li> <li>4.Sludge pasteurization</li> </ol>	<ol> <li>Binder</li> <li>Fiber cement</li> <li>Aerated cellular concrete</li> <li>Bricks</li> <li>Asphalt filler</li> <li>Road construction stabilization</li> </ol>	<ol> <li>Polyethylene filler</li> <li>Zeolite</li> <li>Synthetic lightweight aggregates</li> <li>Rubber filler</li> <li>Phosphate ceramics</li> <li>Inorganic fiber</li> <li>Vitrocrystalline materials</li> <li>Ceramicrete</li> </ol>	<ol> <li>Adsorbent</li> <li>Electrocoagulation optimization</li> <li>Neutralization</li> <li>Extraction</li> </ol>

TABLE 1 ASH APPLICATION AREAS

TABLE 2ELEMENT CONTENT IN ASH

Chemical element	Content in wood ashes, C <sub>mas</sub> %	Content in coalashes,C <sub>mas</sub> , %
Ca	15 (2,5-33)	18 (7-33)
К	2,6 (0,1-13)	1,6 (3-4)
Mg	1,6 (0,5-3,2)	1,2 (1-2)
Mn	0,4 (0-1,3)	1,2 (0,3-1,3)
Р	0,5 (0,1-1,4)	0,9 (0,3-1,4)
Na	0,2 (0-0,54)	0,3 (0,2-0,5)
N	0,15(0,02-0,8)	
Fe	2 (1,6-2,45)	

TABLE 3

ASH CHEMICAL COMPOSITION IN TERMS OF OXIDES

Oxides	Contents in wood ashes, C <sub>mas</sub> ,%	Content in coal ashes, C <sub>mas</sub> ,%
SiO <sub>2</sub>	20-60	40-70
Al <sub>2</sub> O <sub>3</sub>	0,1-12	14-35
Fe <sub>2</sub> O <sub>3</sub>	1,5-5,3	2-20
Fe <sub>3</sub> O <sub>4</sub>	-	2-14
MgO	0,3-5	1-10
Na <sub>2</sub> O	0, 1-0,8	0,1-5
CaO	0,8-43	0,5-30
K <sub>2</sub> O	1-1,8	0,5-3

TABLE 4

THE METAL CONTENT IN ASH

Metal	Content in wood ashes,mg/kg	content in coal ashes, mg/kg
Fe	5000-6000	7000-160000
Zn	350-620	
Cu	87,8-127	
Cr	54-133	2-1100
Pb	20-27	4-230
Cd	3,5-4,9	3-7

It can be seen that in the solid fossil fuel ash composition prevail silicon, aluminum, iron, while the biomass ash composition is characterized mainly with calcium, potassium, magnesium. Wood ashes observed significantly lower content of heavy metals [8,9,22].

The specific direction of the ash application depends on the ash composition and structure. Thus, the ash being used in the production of adsorbents options determine the porosity, pore shape, size and structure, the specific free surface area, adsorption ability and capacity. The paper presents results of wood ash physico-chemical studies

## II MATERIALS AND METHODS

Object of research - wood ash, collected from firewood, consisting mainly of pine, birch wood mixture burned in private home furnaces. Ashes were dried to constant weight in a drying oven at a temperature of  $115-120^{\circ}$ C and screened out through a sieve with a mesh width of 0.5 mm.

Weed out ash color was light gray with small black particles of unburned coal impurities.Experimentally determined ash characteristics:

1. Friable weight - by the direct weighing of the volume of ash, poured into a beaker. Mass of the samples were 20-40g.

2. Mineral mass density–with pycnometer method. Mass of samples were 2-3g.

3. Specific free surface - with methylene blue adsorption method, which is based on the Langmuir adsorption theory equation, which defines the relationship between adsorbed on the surface quantity of molecules mononuclear layer and the amount of the surface. The surface area of the adsorbent surface  $S_f$ , which holds the adsorbed molecules

### $S_f = V \cdot N \cdot CA_m / m \cdot M$

Where:

V- volume of solution use for titration, ml,

C-concentration of the solution

N-Avogardo's number

 $A_{\rm m}$  –square,which occupies one molecule of the substance adsorbed on the adsorbent surface

M-adsorbable substances molecular weight

m- ash sample mass

In an experiment using methylen blue

 $M = 319.9 \text{ g}, Am = 106 \cdot 10^{-20}, m^2, C = 0.03 \text{ g} / 1,$ N=6.023.10<sup>-23</sup>.

The sample of the ash (about 1 mg) was poured in 25 ml of water, then added the sulfuric acid - 5n concentration, mixed and then the suspension was

titrated with 0.3% methylene blue according to the standard method [27].Specific surface area calculations were performed according to the formula

## $S_f = 5.98 \cdot 10^3 V/m, m^2/g.$

4. Loss on heating  $\eta$  - by the direct weighing method. Samples (m<sub>0</sub> = 5 g) were heated in a muffle furnace at a temperature of 850-900 <sup>o</sup>C 2 hours, and then weighed(m<sub>1</sub>):  $\eta$ =m<sub>0</sub>/m<sub>1</sub>

5. One of the most important characteristics of the ash is quantity and composition of soluble components in the ash[28]. The study determined experimentally ash component solubility changes depending on the time of contacting with water. Ash samples - 6 portions each of the 10 g were tipped onto 6 glasses with distilled water 200 ml and suspension was stirred in flocculation device "Armfield" 10, 20, 30, 40, 60, 90 minutes at a temperature of  $20^{\circ}$ C at a speed of 150 RPM. Solutions were filtered, and then were measured: optical density, electrical conductivity, pH, phosphate, nitrate and nitrite contents.

Having regard to soil contamination with heavy metals profound impact on the quality of the environment and ecosystems in all filtrates were determined concentration of heavy metals - the moving soluble phase, which is able to migrate into the soil. Analyzes were performed with a Perkin Elmer atomic absorption spectrometer firm AAnalyst200.

In the ash samples after their flltration and drying was determined specific free surface.

In order to analyze the potential use of ash as adsorbents for wastewater treatment for all ash samples was determined adsorption capacity. For this purpose, the experimental solution was made with six metal ion content.In distilled water were dissolved 0.02 to 0.06 g salts (CuSO<sub>4</sub>, FeSO<sub>4</sub>, MnSO<sub>4</sub>, CrCl<sub>3</sub>, PbSO<sub>4</sub>, CoSO<sub>4</sub>) so that the metal ions in solution should be between 2.5 and 4.5mg/l.

Adsorption ability was investigated as follows: In 7 flasks were poured 200 ml of experimental solution, and 5 g of the ash samples. The flasks were placed on a rotary shaker for 1 hour. After the shaking solution was filtered and in the filtrate was determined the concentration of remaining metal by Perkin Elmer

atomic absorption spectrometer AAnalyst200. Were calculated the absolute amount of adsorbed metal  $m_{ad}$ , solution concentration change  $\Delta C$ , solution treatment of metals degree  $\eta$  and the relative adsorption capacity of 1 gram of ash  $A_n$ .

## **III EXPERIMENTAL RESULTS**

The investigated wood ash mechanical and physical properties are summarized in the Table 5.

TABLE 5
MECHANICAL PROPERTIES OF WOOD ASH

NR	PROPERTIES	RANGE	AVERAGE
1	FRIABLE WEIGHT , G/CM <sup>3</sup>	0,50-0,59	0,53
2	MINERAL MASS DENSITY P <sub>0</sub> ,G/CM <sup>3</sup>	1,74-1,87	1,82
3	POROSITY IN LOOSE PHASE P,%	68-72,3	70,8
4	LOSS ON HEATING H, %	6,9-7,8	7,75
5	$\begin{array}{c} \text{Specific free surface} \\ \text{S}_{\text{f}}\text{,}\text{M}^2\text{/}\text{G} \end{array}$	2,2-2,4	2,25

Specific free surface of filtered ash after extraction of soluble substances is shown in the table 6.

TABLE 6

Rinse time,min	10	20	30	40	90	Sinte- red	Heated in water
Specific free surface S <sub>f</sub> (m <sup>2</sup> /g)	2,9	2,3	2,4	2,9	2,2	2,2	9,6

In the table 7 are results of the filtered ash adsorption efficiency to metals as changes of their concentration in the experimental solution after adsorption.

Adsorption rates were calculated as the concentrations ratio  $\Delta C / C$ . Table 8 summarizes the ash extract physico-chemical properties and Table 9 – metal content of wood ash extracts depending on extraction time.

Metal	Experimental	10min	20min	30min	40min	90min	C <sub>avg</sub>	Adsorption
	solution							rate,%
	(C <sub>0</sub> )							
Cu	2,84	0,12	0,14	0,12	0,14	0,13	0,13	95,4
Co	2,62	0,0	0,01	0,0	0,006	0,0	0,003	99,9
Cr	3,52	0,04	0,06	0,05	0,05	0,04	0,048	98,6
Mn	3,87	0,01	0,016	0,013	0,02	0,006	0,013	99,6
Fe	4,48	0,0	0,03	0,0	0,03	0,0	0,012	99,7
Pb	2,37	0,007	0,035	0,17	0,02	0,01	0,018	99,2

 TABLE 7

 ASH ADSORPTION EFFICIENCY (CONCENTRATION C, Mg/L) TO METALS DEPENDENCE OF MIXING TIME.

Properties	Extract a	Extract after the mixing, min							
	10 20 30 40 60 90 0								
Optical density A,% ,λ=350nm	0,176	0,104	0,097	0,140	0,099	0,083			
λ=760nm	0,019	0,003	0,006	0,019	0,006	0,04	0,015		
Electrical conductivity 6,mS	3,1	3,0	3,0	3,1	3,0	3,2	7,7		
pH	9,9	9,9	9,5	9,6	9,6	9,6	9,9		
Nitrates, mg/l	3,6	2,5	3,2	2,4	2,6	5,9	-		
Nitrites, mg/l	0,15	0,34	0,25	0,18	0,20	0,32	-		
Phosphates, mg/l	1,9	1,4	1,4	1,9	1,0	1,2	-		

 TABLE 8

 THE PHYSICOCHEMICAL PROPERTIES OF ASH EXTRACT

 TABLE 9

 THE METAL CONTENT IN THE WOOD ASH EXTRACT

Mixing	Cu		Co		Cr		Mn		Fe		Pb	
time,	С,	С',	С,	С',	С,	С',	C,	С',	С	С',	С,	С',
min	mg/l	mg/kg										
		ash										
10	0,077	1,54	0,032	0,65	0,223	4,46	0,012	0,24	0,058	1,16	0,018	0,37
20	0,072	1,44	0,033	0,66	0,256	5,13	0,007	0,14	0,007	0,14	0,018	0,36
30	0,113	2,27	0,053	1,06	0,259	5,17	0,018	0,37	0,003	0,06	0,018	0,36
40	0,096	1,92	0,046	0,92	0,368	7,36	0,025	0,49	0,00	0,00	0,021	0,41

## IV DISCUSSION

From the literature data the properties of biomass ash are quite different, which means that each type of biomass, depending on the composition, growth conditions and possible burning regimes may have extensive property variation.

At the same time our experimental data show that the investigated wood ash density, friable weight, loss on ignition is possible properties within a fluctuation band: density range 1.7 to 1.9 g/cm<sup>3</sup> is also characterized by wood and other biomass ash.

Wood ash particles after screening were analyzed visually under a microscope and compared to paper and reed ash obtained in analogous burning conditions (Fig.1).

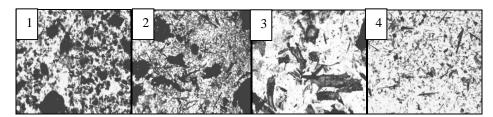


Figure 1. Biomass ash under a microscope: 1 - wood ash, 2- reed ash, 3-paper ash, 4 - reed ash heated at 900 0C

The images show significant differences in the structure of the ash. Wood ash particles have finer shape close to spherical, stick together in clusters.Reed ashes contain the unburned plant cells, the paper ash has more fibrous particles structure. It can be concluded that wood ash must have larger specific free surface, which determines the activity of contact with other substances to be higher.The

measured wood ash free surface  $S_f$  average 2.4 m<sup>2</sup>/gis characterized by the ash of biomass and other fuels, for example the fly ash of coal and lignite ash have  $S_f$  between 2.01 to 5.4 m<sup>2</sup>/g Typically, the ash specific free surface is independent of the flushing time of 10-90 min range (table 6). This means that washing itself without temperature changes practically does not change the pore structure.

Exposure to biomass ash activation can achieve much higher specific free surface values. Thus, as shown in the study [30], rice husk ash additional processing increases the specific surface of 119 m<sup>2</sup>/g. Also, in our experiments ash samples, which were treated in hot water at 90°C increased the specific surface area of up to 9.6 m<sup>2</sup> / g (see the table 6). Typically, the only heating without the presence of water up to 900 °C show that specific surface area remained at 2.2 m<sup>2</sup> / g range.

As already mentioned the soluble component content in ash in many cases determines their using potential areas and restrictions.

This is especially important for heavy metal migration ability in soil from ash. A dangerous situation is possible not only when the ashes are used for improvement of soil, but also in emergency situations. In Greece performed studies of mobile metal ions from the ashes spread of forest fires and their impact on soil and ground water quality [31,32]

Given that in the Latvia quite extensively are burned in spring last year's litter, this question arises in our environment also.

Therefore, in our investigation in ash extracts were determined concentrations of heavy metals

Experiments showed that in the water from ashes were extracted copper, cobalt, chromium, manganese, iron and lead. (Fig.2, Fig.3, Fig 4.) In solutions were did not found nickel and cadmium.

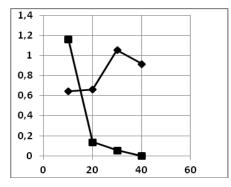


Figure 2. Cobalt and iron concentration C in the water changes depending on the ash flushing time t.

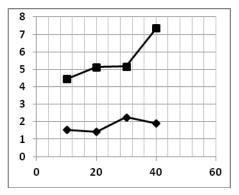


Figure 3. Chromium and copper concentration C in the water changes depending on the ash flushing time t.

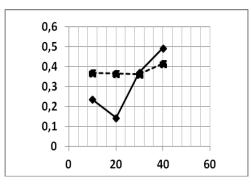


Figure 4. Lead and manganese concentration C in the water changes depending on the ash flushing time t.

In filtrate, where the ashes were heated in at 90  $^{0}$ C, turned out to be significantly higher dissolved metal concentrations.

Thus, the copper concentration in the solution increased 1.27 times, the cobalt -1.73, chromium - 1.27, manganese-1.16 Iron-2.69 lead -1.9 times compared to the maximum concentration of extract at a temperature of  $20^{\circ}$ C (Fig.5).

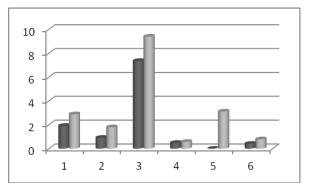


Figure 5. Metal concentration changes in water after heating to  $90^{\circ}$ C in water compared with rinsing at T =  $20^{\circ}$ C. 1 - copper, cobalt 2-3,4-chromium-manganese, 5 - iron, 6 - lead

In these circumstances the nickel (C = 0.06 mg / 1) was found in solution also.

Substantial increasing all the dissolved elements concentrations in the hot water is also confirmed by the solution conductivity enlarging (2 times) and the optical density of high-frequency light wave range (3.7times) increasing.

In ash extracts were found phosphates, nitrates  $NaNO_3and$  nitrites  $NaNO_2$ .Nitrate concentration greater than nitrite concentrations between 13 and 24 times (see table 8.). Typically, the mixing time did not affect significantly the concentrations of the substance, and did not change the pH of the solution (9.7), the specific electrical conductivity (3 mS) and optical density. Ash adsorption capacity were investigated in all ash samples after washing - as a result of the ash were removed soluble components

Solution after the ash adsorption (table 9.) show that from the solution were adsorbed all metals. Extract metals constitute 95.4 to 99.9 percent. Parallel experiment showed that the ash flushing for at least 90 min did not give a significant change in the ash adsorption ability.

But the ashes, which were previously subjected to heating at a temperature of 900<sup>0</sup>C per hour adsorption capacity increased with respect to all metals (Fig. 6).

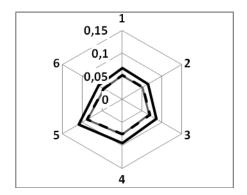


Figure 6. Ash adsorption capacity (mg / g) changes after heating at  $900^{\circ}$ C (solid line) compared with rinsing at T =  $20^{\circ}$ C (dotted line). 1 - copper, 2-cobalt,3 –chromium,4-manganese, 5 - iron, 6 – lead

The obtained experimental data were converted to ash adsorption capacity  $\beta$  - the adsorbed amount of metal per gram mass of ash.

Since on the ash surface in our case absorb all metals was calculated integral ash adsorption capacity for all six metals, which amounted to an average of 0.367 g of metal per 1 kilogram of ash (Fig7).

Note that the metal concentration in solution were relatively low and the total amount of adsorbed metal on ash did not reach maximum saturation. This means that the results

of adsorbent capacity are conditional, but they strongly characterize wood ash as perspective adsorbent.

Apart from the initial concentration of the elements in the experimental solution each metal adsorption capacity  $\beta$  ratio to the metal  $\lambda$ 

 $\lambda = \beta / C_{\rm M} = 0.185$ 

This means that the degree of adsorption within the limits of the carried experiment data is constant and independent of the initial metal concentration

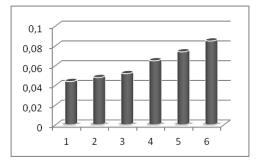


Figure 7. The average mass of the adsorbed metal by wood ash, mg / kg. 1 -lead,2-cobalt, 3-copper, 4-chromium, 5-manganese, 6-iron.

As was shown, ash specific free surface is relatively small in comparison with the specially designed adsorbent specific surface area. This means that despite the high adsorption capacity of the ash capacity is low. There is a need to continue research into the ash to increase the specific free surface and form a specific pore structure of the space optimally suitable physico-chemical adsorption smoothly

## V CONCLUSIONS

Researched wood ash mechanical and physical properties specific free surface, metal content of wood ash in extracts, ash adsorption capacity in connection with metals.

It was found that wood ash density is in the range of 1.74 to 1.87 g/cm<sup>3</sup>, porosity 68-72% in loose phase. It is concluded that even at relatively low - 2.2 -2.4 m<sup>2</sup> / g specific surface free of ash adsorption capacity to metals (Cu, Co, Cr, Mn, Fe, Pb) is quite high. In the experimental solution after adsorption metal concentrations decreased by 95-99%.

Part of metals in ash are in the soluble in water compounds. After stirring ash in water during10-90 min in the extracts were identified metals in concentrations comprised between 0,02 mg / 1 (Mn) up to 0.36 mg/l (Cr). Mixing time did not significantly increase concentrations of metals. The iron concentration in the extract even decreased to 0 after 90 minutes mixing time, which means that the iron changed in insoluble compounds. Cadmium and nickel were not found in the ash extracts. However, after heating the ash in water at  $90^{\circ}$ C gives a significant increase in metal ion solutions - an average of 1.2 to 2.7 times. In addition, in the solution appears nickel.

This means that each kilogram of ash can give in the groundwater up to 2 mg Cu, 7 mg Cr, 1 mg Fe, less than 1mg - Pb, Mn, Co.

Experiments have shown that the ash specific free surface can be increased under pre-preparation, using physical effects to change the spatial pore structure and activate the particle surface adsorption capacity, such as when exposed to hot water.

It can be concluded that the ash is a perspective raw material for production adsorbents and their use have positive effect not only in the traditional farming areas, but is perspective in wastewater treatment technologies as well.

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