WASTE ASHES FROM BURNED SUNFLOWER HULLS AS NEW FERTILISING MATERIALS

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Abstract: *Closing the loop – An EU action plan for the circular economy identified the Fertilisers Regulation revision as a key legislative proposal to boost the market for secondary raw materials. The European Commission has adopted recently EU Fertilising Products Regulation EU 2019/1009 expanding its scope to secondary-raw-material-based products (from biogenic wastes and other secondary raw materials). During the industrial processing of sunflowers, sunflower husks used as alternative fuels resulting in the generation of waste ash. Sunflower ash is a known material as a good and cheap source of potassium. In present study the tested samples of ashes is characterized as a starting raw material for the producing fertilizers in an accredited and authorized Laboratory for fertilisers quality. The tested samples is not loaded with heavy metals and the risk of recycling contaminants has not been assessed. According to the content of available (water-soluble) elements, the content of soluble phosphorus and micronutrients is very low, while potassium is completely water-soluble (40 to 50% K_2O m/m), therefore, the tested ashes can be regarded as a good raw material as a source of potassium component in the final product. The pH reaction of the samples is extremely alkaline, therefore it is necessary to neutralize pH reaction in the industrial processing of this raw material, or to restrict the final product for use on acid reaction soils.*

Keywords: *Circular economy, Sunflower oil industry, Biogenic industry waste, Sunflower hulls ash, Fertilizers*

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1. INTRODUCTION

Closing the loop – An EU action plan for the circular economy, as adopted by the European Commission, identified the Fertilisers Regulation revision as a key legislative proposal to boost the market for secondary raw materials, and the revised Waste Framework Directive establishes ambitious targets for recycling.

The European Commission has adopted recently EU Fertilising Products Regulation EU 2019/1009 (2019) expanding its scope to secondary-raw-material-based products (from biogenic wastes and other secondary raw materials). The new Regulation defines equal conditions for all products (fertilizers) in the EU and additionally promotes the use of secondary – recycled raw materials.

In the same year was created Report (Huygens et al. 2019) which explores a possible legal framework for the manufacturing and placing on the market of specific safe and effective fertilising products derived from biogenic wastes and other secondary raw materials. The report contains technical proposals on eligible input materials, process conditions, quality requirements as well as quality management system requirements. Additionally, the report assesses the possible impacts in order to shed a light on the added value that these fertilising materials could provide for food security, food safety, environmental protection, and the European fertilising and agricultural sector.

Numerous research studies have been carried out analysing the pyrolysis and firing processes of natural organic wastes as a renewable and environmentally friendly energy source (Quaranta et al. 2011).

Fertilizer quality is regulated within the Republic of Serbia by the Law on plant nutrition products and soil conditioners OGS 41/2009 (2009) and OGS 17/2019 (2019), and the by-laws adopted for its implementation, such as Regulation OGS 30/2017 (2017) and OGS 31/2018 (2018). This Regulation of the Republic of Serbia is harmonized with Regulation EU 2003/2003 (2003) (Technical requirements for mineral fertilizers and inorganic soil conditioners) in the area of classification and labelling of final products - fertilizers.

During the industrial processing of sunflowers, sunflower husk is primarily used as animal feed (Quaranta et al. 2011), and it can also be used as an energy source as alternative fuels (May et al. 2017) resulting in the generation of waste ash. Ash has long been recognized as a soil improver and plant growth enhancer. In the 18th century, the ash obtained by burning wood was used to obtain potassium carbonate. Back in 1790, the first industrial process to be patented in the US was making fertilizer from ashes. As cheaper sources of lime and potash for fertilizer were later discovered, the ash market died down. Sunflower husks ash is a known material as a safety, good and cheap source of potassium (Paleckienė et al. 2010).

The aim of this study was characterization of sample of ashes from burned sunflower hulls as a starting raw material for the industrial process of producing fertilizers according to the current legislation.

2. MATERIAL AND METHODS

In present study the samples of ashes were tested from two oil mill factory (Dijamant Zrenjanina and Bimal Brčko distrikt). The material was obtained after collecting the ash from special incineration plant with the electrostatic filter (**Figure 1**). The ash is collected in a receiving container, and can be further collected in jumbo bags and transported by trucks to future processing into fertilizer.

Figure 1. Facility and electrostatic filter where ash is collected, Dijamant Zrenjanin

All laboratory analyses were performed at the Laboratory for Soil and Agroecology of the Institute of Field and Vegetable Crops, Novi Sad, Serbia, accredited according to the standard ISO/IEC 17025 (2017) and authorized institution for fertilisers quality and registration.

The following standards and analytical methods were applied, according to Regulation OGS 30/2017 (2017), 31/2018 (2018), and Regulation OGS 84/2017 (2017):

- Moisture content: gravimetric method;
- pH value (in H_2O and 1M KCl): potentiometric method;
- Nitrogen (total): CNS elemental analysis by Elementar analyser VARIO El III;
- Phosphorus (water soluble): spectrophotometrically;
- Phosphorus (total): ICP method, ICP-OES Vista Pro Varian, after MW digestion by Milestone ETHOS;
- Potassium (water soluble and total): flame photometry;
- Trace elements and secondary elements Ca, Na, Mg, Fe, Mn, Cu, Zn, (water soluble and total): ICP method, ICP-OES Vista Pro Varian;
- Heavy metals (total) As, Cd, Cr, Ni, Pb (total): ICP method, ICP-OES Vista Pro Varian, after MW digestion by Milestone ETHOS;
- Hg (total): by DMA 80 Direct Mercury analyzer, Milestone.

3. RESULTS AND DISCUSSION

Since in R. Serbia lacks a legislative framework for the quality of input raw materials for fertilizer manufacturing, sunflower husk ash is characterized according to the criteria for finished fertilizer products. These criteria are prescribed in two extensive regulations with annexes (OGS 30/2017 and 31/2018, and OGS 84/2017). These regulations prescribe the keys to the classification of fertilizers with a series of restrictions, in order for the

end product to be primarily safe for use and the agroecosystem, and on the other hand, to contain a sufficient amount of nutrients in terms of consumer protection and a real effect on plant growth.

Based on the obtained results, the tested material has a favorable moisture content of only up to 2% moisture (**Table 1**). When using other types of biowaste materials as potential fertilizers, the high moisture present is most often a limiting factor and such materials need to be additionally dried.

The pH reaction, both active (in H_2O) and substitution reaction (in 1 M KCl), is extremely alkaline and ranges from 11 to 12.64 pH units (**Table 1**). Potassium, calcium, and magnesium carbonate or oxides are present in comparatively large quantities giving the ashes a strongly alkaline reaction. The obtained high pH reaction is a limiting factor for the application of fertilizers on all types of soil and must be limited to application only on soils with a significantly acidic reaction (up to pH=6).

3.1. Major nutrients NPK

In terms of total nitrogen content, it is at a negligible level and this material cannot therefore be considered a nitrogen-containing fertilizer (**Table 1**).

According to the total content of primary macronutrients (NPK), the tested sample showed a high content of phosphorus and potassium as nutrients. According to the content of available (water-soluble) phosphorus and potassium, the content of soluble phosphorus is very low, while potassium is almost completely water-soluble (**Table 1**). The criterion for fertilizer quality is the bio-accessible nutrient content, so that they can be taken up by the root system. Based on this part of the research, the tested sample can be regarded as a good raw material as a source of potassium component in the final product – plant nutrition product - fertilizer.

Table 1. Moisture, pH and NPK content of tested ashes samples

PARAMETER	DIJAMANT	BIMAL
Moisture content, %	0.400	1.630
pH (H_2O)	12.64	11.07
pH (KCl)	12.46	11.00
Total N, %	0.16	0.18
Total P_2O_5, %	10.42	4.90
Total K_2O, %	42.85	55.30
Water-soluble P_2O_5, %	0.02	0.23
Water-soluble K_2O, %	38.75	52.70

3.2. Microelements

Similar to major nutrients, the total content of micro elements is high, while their accessible content (water soluble content) is very low (**Figure 2** and **Figure 3**).

The content of Ca and Na (and partially Mg) is considered here as a limiting factor because they can lead to soil degradation, alkalization and salinization in case of high concentrations and excessive application. Lack of these elements is very rare in soils.

Essential microelements Cu, Fe, Mn and Zn, are desirable in fertilizer and have a favorable effect on the growth and development of plants. However, based on this part of the research, their accessible (water-soluble) content is too low to consider the tested material suitable for fertilizers with the addition of microelements (**Figure 3**).

3.3. Heavy metals

In order for a material to be safe for use as a fertilizer, it must not contain dangerous and harmful substances. This is the first analysis that is tested in the laboratory for fertilizer characterization. According to the methodology, it tests the total content of heavy metals, because even these insoluble fractions can pollute the soil over time.

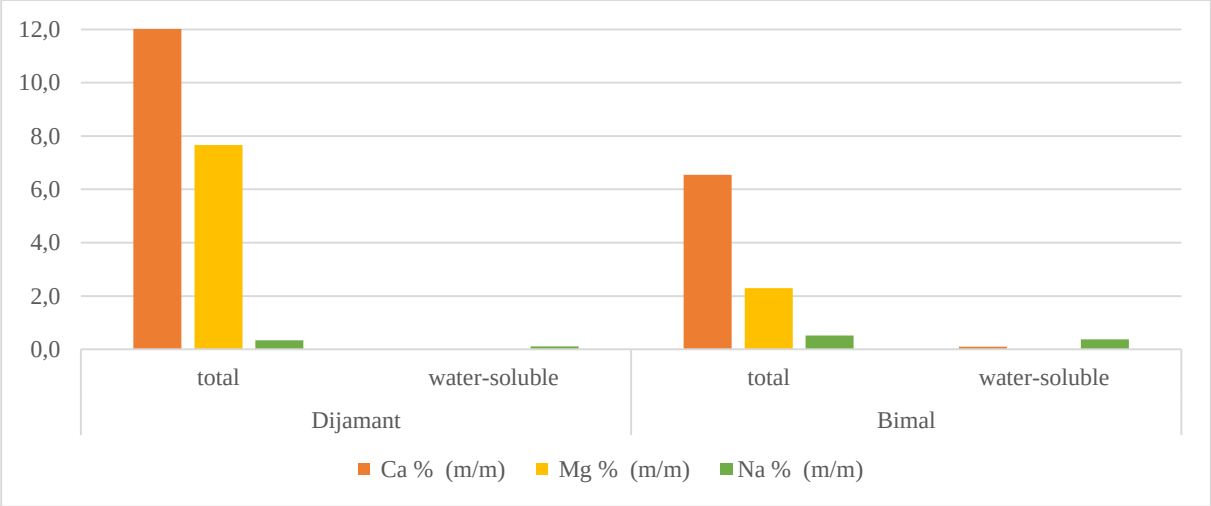

Figure 2. Total and water-soluble content of Ca, Mg and Na of tested ashes samples

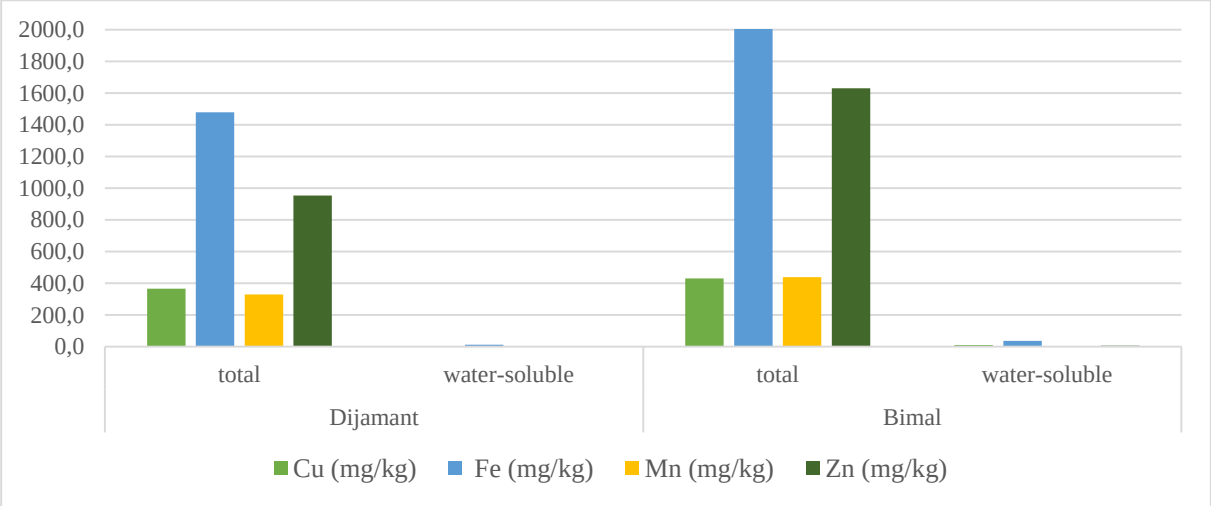

Figure 3. Total and water-soluble content of Cu, Fe, Mn and Zn of tested ashes samples

Table 2. Total heavy metals content of tested ashes samples

HEAVY METAL	DIJAMANT	BIMAL	MAC
As, mg/kg	< MDL (2.0)	< MDL (2.0)	/
Cd, mg/kg	< MDL (1.5)	< MDL (1.5)	3.0
Cr, mg/kg	4.9	68.0	100.0
Ni, mg/kg	40.3	27.9	100.0
Pb, mg/kg	< MDL (2.0)	< MDL (2.0)	100.0
Hg, mg/kg	< MDL (0.001)	< MDL (0.001)	1.0

MDL - Method detection limit
MAC - Maximum Allowed Concentration

Based on this part of the research, all samples meet the criterion of being below the prescribed limit of the maximum allowed concentration (**Table 2**). The contents of As, Cd, Ni, Pb and Hg, as plant xenobiotics, were very low, below detection limits. Certain amounts of Ni and Cr were determined, because these are biogenic elements that are an integral part of the sunflower plant and husk. The content of these elements must be continuously monitored, so that they do not exceed the set limits and thus potentially pollute the soil.

4. CONCLUSION

The tested sample of ashes from burned sunflower hulls is not loaded with dangerous and harmful substances and meets the requirements as a starting material for the industrial process of fertilizer production as a good source of potassium component, with the optimization or specification of the pH reaction of the final product in the technological process.

pH reaction of the tested samples is extremely alkaline, as well as the content of total calcium and magnesium, therefore it is necessary to neutralize pH reaction in the industrial processing of this raw material, or to specify the final product (instructions for use) for use on acid reaction soils as a special product for the improvement (calcification) of acid soils.

5. FUTURE STEPS

For recycling biogenic waste, networking is needed made up of scientific institutions, technological experts and industry factories, especially in the food industry sector. It is necessary to assemble a multidisciplinary team of agrochemists, material technologists and process industry experts. Research on the topic of using industrial waste as a raw material for fertilizers is very current and suitable for project financing.

The limitations are numerous, from the lack of infrastructure for material manipulation, the high heterogeneity of waste material, material granularity (Paleckienė et al. 2010) to the placement of the final product. However, due to the topicality and importance of biogenic waste recycling, in this green transition process should be start as soon as possible.

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