

Article

Studies on the Possibilities of Processing Buckwheat Husks and Ash in the Production of Environmentally Friendly Fertilizers

Odeta Pocienė *  and Rasa Šlinkšienė 

Department of Physical and Inorganic Chemistry, Kaunas University of Technology, Radvilenu St. 19, LT-50270 Kaunas, Lithuania; rasa.slinksiene@ktu.lt

* Correspondence: odeta.pociene@ktu.lt

Abstract: The sustainable utilization of different food waste and other products is one of the challenges of the European Green Course. Buckwheat has major potential as a food ingredient; however, processing buckwheat into food products generates a large amount of solid waste that needs to be sustainably disposed of. The by-products that come from the processing of the buckwheat contain high contents of carbon and hydrogen and can be used as raw materials for the production of granular biofuels. This work proposes and explores the potential of a different route of buckwheat husk ash utilization. Chemical analysis of the buckwheat husk ash (BHA) and uncleaned buckwheat husks (UBH) showed significant amounts of primary and secondary nutrients ($0.28 \pm 0.06\%$ – $5.84 \pm 0.43\%$ P_2O_5 ; $4.56 \pm 0.46\%$ – $38.63 \pm 1.82\%$ K_2O ; $0.09 \pm 0.01\%$ – $12.18 \pm 0.38\%$ CaO and $0.47 \pm 0.08\%$ – $3.56 \pm 0.18\%$ MgO) as well as micronutrients (Zn, Mn, Cu, and Fe) and carbon ($29.53 \pm 0.50\%$ – $54.35 \pm 0.58\%$ C). It has been determined that granular biofertilizers can be produced by using drum granulators from the mixture of raw materials in an 80–20% BHA, 20–80% UBH, and 10% polyvinyl acetate (PVA) solution. However, when more than 20% of the UBH is present in the raw material mixture, the humidity of granules is high (more than 6%), and bulk density is low (less than 450 kg/m^3). The pH values of 10% solution of the produced granules range from 12.0 to 9.7; thus, the fertilizers can act as a liming agent, which can be recommended for acid soils. This suggests a potential for a cradle-to-cradle type of regenerative engineering process design, where the end product of buckwheat processing—buckwheat husk ash and untreated buckwheat husks—can be returned back to the soil to replenish the nutrients, resulting in an overall sustainable process.



Citation: Pocienė, O.; Šlinkšienė, R. Studies on the Possibilities of Processing Buckwheat Husks and Ash in the Production of Environmentally Friendly Fertilizers. *Agriculture* **2022**, *12*, 193. <https://doi.org/10.3390/agriculture12020193>

Academic Editors: Othmane Merah, Purushothaman Chirakkuzhyil Abhilash, Magdi T. Abdelhamid, Hailin Zhang and Bachar Zebib

Received: 28 December 2021

Accepted: 26 January 2022

Published: 30 January 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

Keywords: ash; buckwheat husks; chemical composition; granulated fertilizers; properties

1. Introduction

Buckwheat has major potential as a food ingredient since it contains proteins of high nutritional value, dietary fiber, starch, rutin, *D-chiro*-inositol, vitamins, and minerals [1,2]. The consumption of buckwheat protein has been shown to lower plasma cholesterol [3]. While currently underutilized due to its lower yields compared to wheat and other cereals, it has recently sparked a new interest due to the possibility of using it to recover the marginal areas [4]. Buckwheat can be planted in various soil types, including infertile and poorly tilled areas [5]. Importantly, it can also help to manage nutrient balance by acting as a phosphorus scavenger due to its high capability of absorbing soil phosphorus [4]. In 2019, world production of buckwheat was 1.6 million tons, led by Russia with 48% of the world total, followed by China with 27% and Ukraine with 3% (FAOSTAT numbers) [6]. The processing of buckwheat into food products also generates a large amount of solid waste that needs to be sustainably disposed of.

Thus far, the sustainable utilization of buckwheat husks, which is a primary processing waste, has focused on the extraction of rutin, a well-known bioactive polyphenol, followed by husk carbonation to yield char. Moreover, it is used in the production of therapeutic mattresses and cushions [7,8]. In principle, buckwheat husks can be used in the food

industry. For example, the utilization of buckwheat husks for the preparation of buckwheat husk tea was proposed [9]. The by-products from the processing of the buckwheat contain high contents of carbon and hydrogen and can be used as raw material for the production of granular biofuels [8]. A significant improvement of up to 50% in greenhouse gas emissions was estimated over gasoline, showing significant sustainability implications of utilizing wheat products for 2nd generation biofuel production [10]. The utilization of wheat (including, but not limited to, rice) husk ash in general has attracted a significant amount of attention due to the very large amounts generated via combustion processes. Typically, about 10% of husks are separated from the grain, and if these husks are combusted, they yield approximately 10% ash. By far, the most explored options of husk ash utilization include its use as a porous absorbent material, while other applications, including as construction materials, have not gained sufficient popularity [11].

Significant amounts of primary and secondary nutrients (P_2O_5 , K_2O , CaO , and MgO), as well as micronutrients (Zn, Mn, Cu, Fe, Co, and Mo), have been detected by chemical analysis of the buckwheat husks ash. This suggests a potential for a cradle-to-cradle type of regenerative engineering process design [1,2,12] where the end product of the buckwheat processing of the husk ash can be returned back to the soil to replenish the nutrients, resulting in an overall sustainable process. The sustainable use of solid waste in agriculture is of crucial importance, and prior attempts have also been made to recover the micronutrients [13].

This work explores and proposes the potential of a route for utilization of buckwheat husk ash and other biomass from the waste of buckwheat groat production. The aim of this work was to study the chemical and crystallographic composition of the buckwheat husk ash and uncleaned buckwheat husks, to create granulated fertilizers by performing laboratory-scale granulation experiments, and to explore their properties.

2. Methods and Materials

2.1. Materials

Wastes from the production of buckwheat groats in JSC “Ekofrisa” (Prienu district, Lithuania) were used as the main raw materials: buckwheat husk ash (BHA) and uncleaned buckwheat husks (UBH). The emulsion of polymer polyvinyl acetate (PVA), which is non-toxic or has a very low level of toxicity when ingested and is questionably carcinogenic, was used as a binder [14]. Analytical grade chemicals and distilled water as a solvent were also used, where necessary, in the chemical analysis.

2.2. Analyte Preparation

A solution for chemical analysis was prepared from BHA and UBH by dissolving the substances in water and hydrochloric acid for 24 h. The resulting solutions were filtered to separate insoluble components; they were then diluted to a known volume and used for analysis.

2.3. Chemical Analysis

Total nitrogen (N) was determined by the Kjeldahl method with the mineralizer Turbodog TUR/TVK, automatic system Gerhardt Vapodest 45s (C. Gerhardt GmbH & Co. KG, Koenigswinter, Germany), using 96% sulfuric acid according to the DIN EN ISO 9001. The essence of the method is that the analyte is distilled into a boric acid solution, while the concentration is determined by the results of the titration with HCl (the accuracy of the method is 0.5%). Three replicates were performed, and the difference in concentration between test results did not exceed 0.5%.

Concentrations of calcium (recalculated as CaO) and potassium (recalculated as K_2O) in BHA and UBH were measured using flame photometry and a PFP-7 from Jenway (Cole-Parmer Ltd., Staffordshire, UK). The flame was produced by burning the mixture of natural gas and air at 1500–2000 °C. Calcium and potassium concentrations were determined at 622 nm and 766 nm wavelengths, respectively, using calibration curves,

which were prepared based on the known concentration of aqueous solutions of the corresponding salts.

The concentration of phosphorus (recalculated as P_2O_5) in BHA and UBH was determined by the photocolometric method by complexing with molybdenum and measuring UV-VIS absorption of the corresponding solution at $\lambda = 440$ nm. T70/T70+ spectrophotometer from PG Instruments Limited (PG Instruments Limited, Lutterworth, UK) was used in all measurements.

Concentrations of calcium (recalculated as CaO) and magnesium (recalculated as MgO) were determined by complexometric titration using different indicators (chalcone carboxylic acid and dark blue chromogen) and titrating against trilon B solution.

The concentration of total organic carbon (TOC) in raw materials was determined by the dichromate oxidation of the organic matter method [15].

Organic matter content was determined according to the modified LST EN 13039: 2012 standard. The samples for the analysis were dried, weighed to within ± 0.001 g and burned for 1 h at 900 °C temperature. The amount of organic matter in the samples was calculated from the weight loss.

Content of iron (Fe), copper (Cu), zinc (Zn), manganese (Mn), cobalt (Co), molybdenum (Mo), cadmium (Cd), lead (Pb), mercury (Hg), nickel (Ni), chromium (Cr), silicon (Si) in BHA and UBH was measured using the AAAnalyst 400 atomic absorption spectrometer (AAS) from PerkinElmer (PerkinElmer, Waltham, MA, USA). The flame was obtained by burning acetylene (7.5 L/min), except when measuring molybdenum (N_2O was used). A mixture of acetylene gas and air (10 L/min) was used to atomize samples.

2.4. Instrumental Analysis

X-ray diffraction analysis (XRDA) of BHA and UBH was performed using Bruker AXS operating at the tube voltage of 40 kV and tube current of 40 mA. The X-ray beam was filtered with a Ni filter to select the $CuK\alpha$ wavelength. The step size was 0.05° and the dwell time was 0.5 s, anodic voltage $U_a = 40$ kV; strength of the current $I = 40$ mA. Data were analysed using a Crystallographica Search-Match Version 2, 1, 1, 1 program.

Fourier-transform infrared spectroscopy (FT-IR) was performed using Spectrum GX spectrometer from Perkin Elmer (PerkinElmer, Waltham, MA, USA) operating in transmission mode. Samples were prepared by pressing a pellet of BHA or UBH and optically pure dry KBr. The final spectrum is shown in a transmittance mode.

Simultaneous thermal analysis (STA) was performed using the thermal analyser LINSEIS STA PT-1000 (Linseis Messgeraete GmbH, Selb, Germany). The parameters that were used for obtaining the DSC–TG curves are as follows: heating rate— 10 °C/min, range— 25 – 700 °C, crucibles—extruded aluminum, atmosphere in the furnace—nitrogen 20 mL/min, measurement accuracy ± 3 °C.

2.5. Granulation

BHA- and UBH-based fertilizers were granulated using a laboratory-scale drum granulator (JSC Arvi fertis, Marijampolė, Lithuania) shown in Figure 1. This granulator is a scaled-down version of a commercially available drum NPK fertilizer granulator. Briefly, a granulator tilt angle with respect to horizontal was 3° , while the rotation speed was 26 rpm. The temperature in the drum granulator was maintained at 60 – 70 °C by blowing hot air.

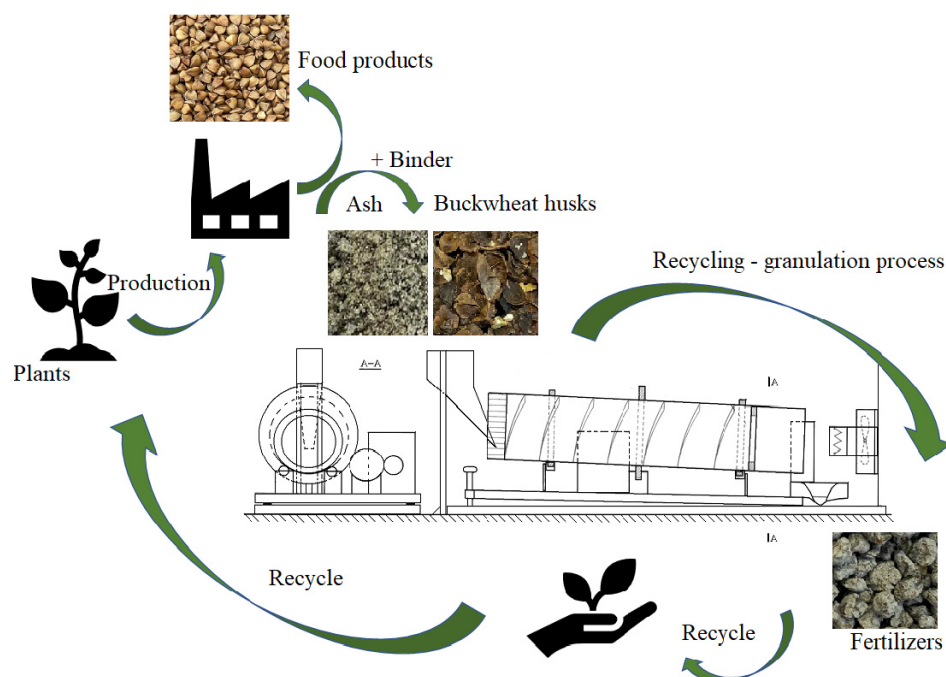


Figure 1. Process of production of environmentally friendly fertilizers.

2.6. Physical Analysis

One of the key fertilizer granule properties, i.e., granule humidity, was determined using a Kern MLS moisture analyzer from Kern & Sohn GmbH (Balingen, Germany), with an accuracy of 0.001 g, after heating the sample to a constant mass at 120 °C.

The granule size distribution of the granulated fertilizers obtained from BHA and UBH was determined while using DIN-ISO 3310/1 sieves from Retsch. (Retsch GmbH, Haan, Germany) The mass of every size fraction was determined by weighing on a WPS 210/C Kern ABJ balance with an accuracy of 0.001 g.

The pH meter pH 211 from Hanna Instruments (Woonsocket, RI, USA) was used in all measurements. The pH was determined for the aqueous 10% BHA, UBH or granular fertilizer solutions; the needed mass was weighed on a WPS 210/C Kern ABJ balance. The resulting suspension was filtered, and pH was measured.

The loose bulk density of granules is a critical property for transportation purposes. Loose granule bulk density was measured using a graduated 100 mL cylinder filled with granules.

The crushing strength of granules is a measure of their resistance to deformation or fracture under pressure. It is a crucial parameter in estimating the expected handling and storage properties of the obtained granular material. The granule crushing strength was determined by applying a constant force until the granule lost its structural integrity [16] using ИПГ-1М (АО “УНИХИМ с ОЗ”, Yekaterinburg, Russia). In particular, 20 granules were analysed, and an average crushing strength value was obtained. The equipment consists of an automated press control by a stepping motor that can apply a force from 5 N to 200 N with an error of $\pm 2\%$ at 20 ± 5 °C.

The hygroscopicity of the granulated BHA and UBH fertilizers was measured by using saturated aqueous sodium nitrite (NaNO_2) solution and water. The typical procedure involved maintaining sample granules in a desiccator for 2 weeks in the presence of saturated NaNO_2 solution at 70%–75% relative humidity and 20–23 °C, and water at 100% relative humidity and 20–23 °C.

2.7. Statistical Data Analysis

Statistical analysis of the results was carried out using MS Excel data analysis (Anova, descriptive statistics) tools, calculating a range of statistical parameters for every data set.

In the case of assessing the chemical composition of the plant nutrients' micro-elements, heavy metals and properties of the granulated product, the value of the standard deviation was given. To analyse and evaluate data, in accordance with the results of the descriptive statistics, the relative (RSD), standard (SD) and absolute (ASD) deviations were calculated at 95% probability. In all cases, the significance level was $p \leq 0.05$. Depending on the method's accuracy, the investigation of the properties of the same sample was performed 3–20 times, and the arithmetic mean of the determined values is presented in this study.

3. Results and Discussion

3.1. The Chemical and Structural Composition of the Buckwheat Husks Ash and Uncleaned Buckwheat Husks

Chemical and functional group composition of BHA and UBH, phase, endo- and exo-effects were determined using different methods, and the results obtained are presented in Table 1 and Figures 2–4. The chemical composition is needed for the assessment of the nutrient composition contained within the raw materials and their potential usability as a granulated fertilizer. As seen from the elemental analysis data (Table 1), a rather large concentration of the primary macronutrient potassium is present in BHA at 35.92% and 38.63% concentration, respectively, as soluble in water and soluble in hydrochloric acid.

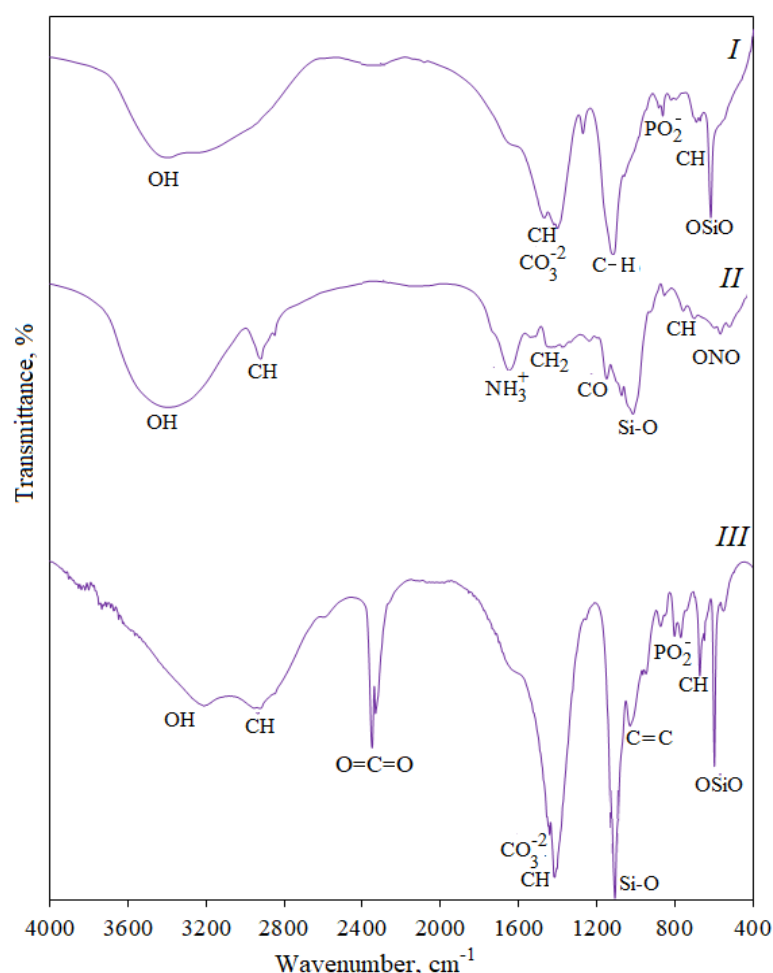


Figure 2. FT-IR spectrum: I—BHA; II—UBH; III—granulated fertilizers (Sample 12).

Table 1. Concentrations of primary and secondary macronutrients, microelements and heavy metals in raw materials.

Sample	Primary and Secondary Macronutrients, %											
	N	K ₂ O		P ₂ O ₅		CaO		MgO		C		
		W	HCl	W	HCl	W	HCl	W	HCl			
BHA	–	0.66 ± 0.09	35.92 ± 1.62	38.63 ± 1.82	0.30 ± 0.06	5.84 ± 0.43	0.17 ± 0.05	12.18 ± 0.38	0.92 ± 0.39	3.56 ± 0.18	–	29.53 ± 0.50
UBH	–	2.28 ± 0.27	4.56 ± 0.46	7.60 ± 0.21	0.28 ± 0.06	0.41 ± 0.05	0.09 ± 0.01	0.29 ± 0.07	0.47 ± 0.08	0.88 ± 0.09	–	54.35 ± 0.58
Microelements, mg/kg												
Sample	Zn		Mn		Cu		Fe		Co		Mo	
	W	HCl	W	HCl	W	HCl	W	HCl	W	HCl	W	HCl
BHA	–	541.13 ± 2.86	–	547.88 ± 1.64	–	385.63 ± 2.56	–	1331.25 ± 0.93	–	7.60 ± 0.06	–	9.30 ± 0.13
UBH	16.13 ± 0.15	86.63 ± 1.01	15.13 ± 0.40	28.63 ± 0.39	–	3.50 ± 0.22	0.88 ± 0.04	212.38 ± 0.92	–	–	–	–
Heavy Metals, mg/kg												
Sample	Cd		Pb		Hg		Cr		Ni		Si	
	W	HCl	W	HCl	W	HCl	W	HCl	W	HCl	W	HCl
BHA	–	1.80 ± 0.09	–	2.88 ± 0.19	–	0.01 ± 0.008	58.25 ± 0.72	76.63 ± 0.74	–	15.70 ± 0.89	–	8.03 ± 0.35
UBH	–	–	–	–	–	–	–	–	–	–	–	–

W—soluble in water. HCl—soluble in hydrochloric acid.

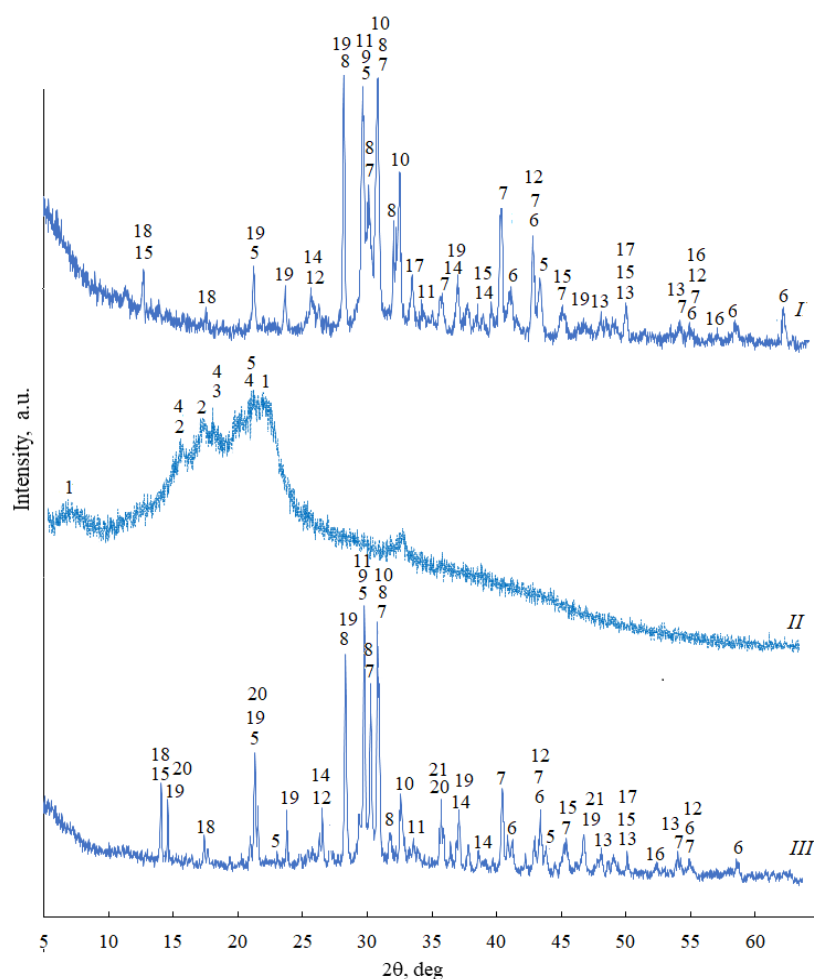


Figure 3. XRD data: *I*—BHA; *II*—UBH; *III*—granulated fertilizers (Sample 12): 1— $C_{36}H_{70}CaO_4$; 2— Zn_3FeCN_6 ; 3— $C_{36}H_{52}O_2$; 4— $Cu(H_2PO_3)_2$; 5— SiO_2 ; 6— MgO ; 7— K_2MgSiO_4 ; 8— $FePO_4$; 9— $K_5P_3O_{10}$; 10— K_2CO_3 ; 11— $CuPO_3F$; 12— $Mg_{0.97}Al_{0.03}O$; 13— CaO ; 14— Al_8Cr_4E ; 15— $Al_6O_{13}Si_2$; 16— Fe_2O_3 ; 17— $CaMnO_{2.65}$; 18— $KNiS_2$; 19— K_2SO_4 ; 20— $KMnFe_3$; 21— Na_2CS_4 .

Concentrations of water-soluble nitrogen and phosphorus in the ash were insignificant; the concentration of hydrochloric acid-soluble P_2O_5 (5.84%) was higher. Furthermore, significant concentrations of hydrochloric acid-soluble secondary macronutrients, including calcium (CaO) and magnesium (MgO), were determined to be 12.18% and 3.56%, respectively. In UBH, concentrations of nitrogen and phosphorus were 2.28% and 0.28%–0.41%, respectively (higher concentrations of hydrochloric acid-soluble macronutrients). Concentrations of water-soluble and hydrochloric acid-soluble secondary macronutrients (CaO and MgO) in the UBH were insignificant. In both raw materials, high carbon concentration was detected. BHA had 29.53% carbon, and the content of carbon in UBH was almost twice as much, i.e., 54.35%.

The data for the microelements necessary for the plants, such as Zn, Mn, Cu, Fe, Co and Mo, are presented in Table 1. Notable concentrations for zinc, manganese, iron, and copper were detected. As seen from the data for the concentration of heavy metals, such as cadmium, lead, mercury, etc. (Table 1), significant concentrations were found only for chromium, nickel and silicon, which are not toxic or hazardous to the environment or plants. The data of the chemical analysis in most cases are in accordance with the data published in the literature [17] (the highest concentrations of potassium, calcium and trace elements like iron, zinc and manganese, which are the main nutrients, were determined). However, there are insignificant differences that can be explained by the fact that buckwheat was grown in different places and under different conditions.

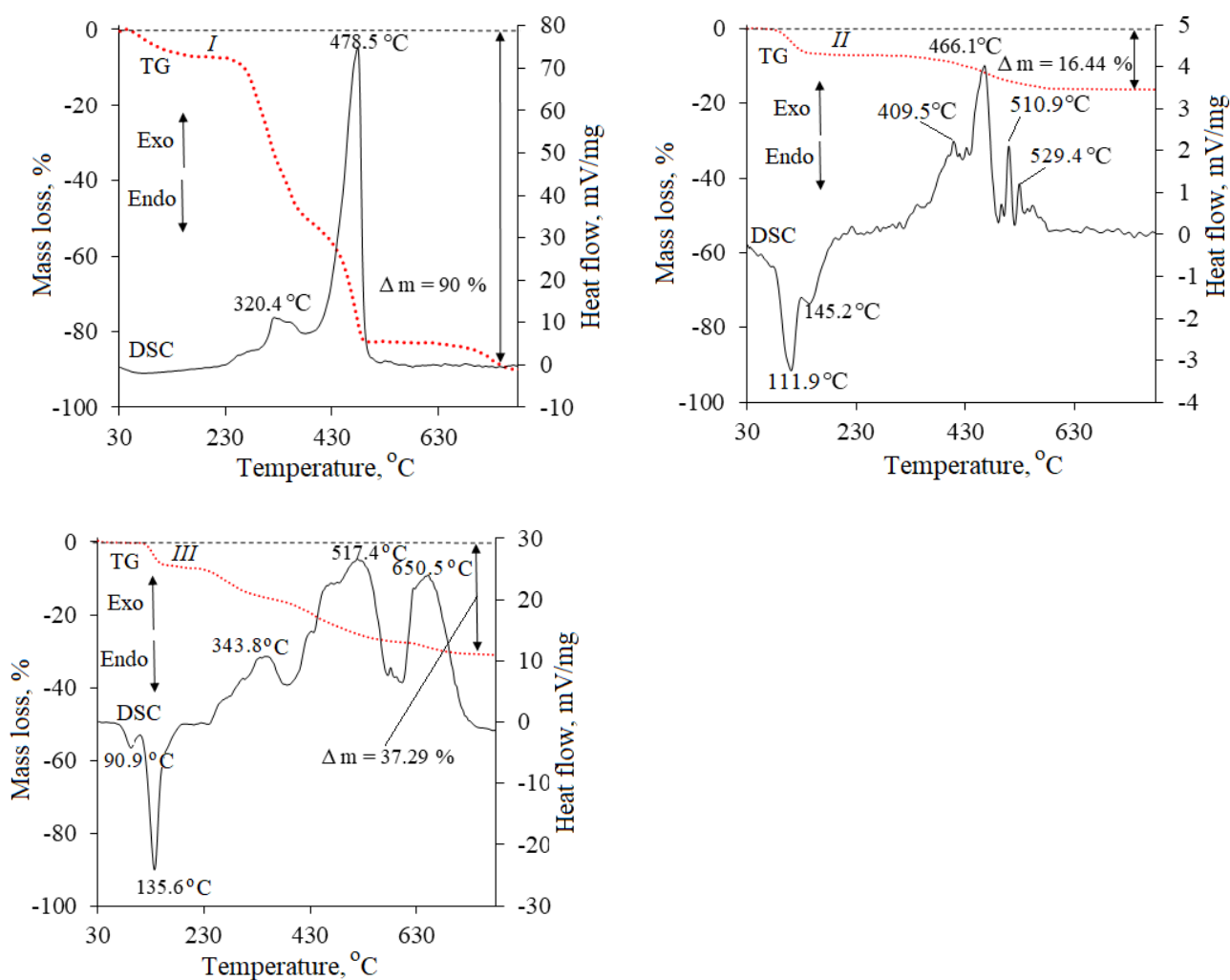


Figure 4. STA data: (I)—BHA; (II)—UBH; (III)—granulated fertilizers (Sample 12).

The total content of organic matter in the raw materials was also measured by burning raw materials for 1 h at 900 °C. It was found that organic matter made up 23.3% of BHA and 98.3% of UBH. The relatively high content of organic matter in the ash from the biofuel boiler plant suggests that its temperature is below 900 °C.

IR spectra of BHA and UBH are presented in Figure 2. In particular, FT-IR ash (I curve) and husk (II curve) analysis has revealed the presence of the same broad peak at 3300–3500 cm^{-1} due to the hydrogen-bonded hydroxyl (O–H) groups.

The IR spectrum of UBH (II curve) displays a peak centred around 2900 cm^{-1} due to the aldehyde (CH) group and a peak in the range of 1500–1630 cm^{-1} due to the NH_3^+ symmetric and asymmetric vibrational motion and saturated aldehyde (C=O). According to the literature [18], a doublet in the 1500–1200 cm^{-1} region can be assigned to the CO_3^{2-} functional group in metal carbonates and to the CH and CH_2 groups. Other complementary peaks (I and II curves) located in the 700–1000 cm^{-1} region can be assigned to C–H bonds and the PO_2^- functional group. The IR spectra have a peak centred around 600 cm^{-1} due to the OSiO group (BHA–I curve) and ONO group (UBH–II curve) [19–23].

In the XRDA curve of BHA (Figure 3, I), a complex set of peaks is observed. These peaks were assigned to several common minerals, including hematite, mullite, potassium phosphorus oxide, magnesium aluminum oxide, and siliceous oxide using SearchMatch1 database data.

These results are very complementary to those inferred from the FT-IR absorption spectrum shown in Figure 2. After combining XRD and FT-IR data, the results indicate that

BHA is comprised of inorganic mineral oxides, phosphates and carbonates. It is important to note that the different XRDA curves of biomass ash and identifiable substances in the different sources vary depending on their origin (biomass type, bottom or fly ash), but the overall carbonates, phosphates, oxides predominate in the ash XRDA spectrum [24–26]. The major diffraction peak of UBH (Figure 3, curve II) occurs within the 2θ scale ranging between 15° and 25° as the compounded peak: $C_{36}H_{70}CaO_4$ (PDF 37–1684); Zn_3FeCN_6 (PDF 75–1257); $C_{36}H_{52}O_2$ (PDF 34–1684); $Cu(H_2PO_3)_2$ (PDF 71–675); SiO_2 (PDF 27–605). The character of the peaks mentioned indicates an amorphous structure and partially correlates with the XRD spectrum of cellulose [27].

Since superheated water vapor can be used as a liquid phase in the industrial production of granular fertilizers and the produced granules have to be dried, the raw materials used in the production of fertilizers must be thermally stable up to approx. $350^\circ C$. STA was performed to evaluate the thermal stability of BHA and UBH, and its results are presented in Figure 4. The HBA curve (I) in Figure 4 shows that an insignificant exo-effect was found in ash at $320.4^\circ C$, and a very high exothermic effect took place at $478.5^\circ C$. This high effect can be explained by the oxidation of unburned organic matter remaining in the ash. This statement is also confirmed by the results of the chemical analysis, since 29.53% of carbon was detected. Therefore, it can be assumed that the operating mode of the biomass boiler is not optimal, and some unburned organic matter remains. The mass loss, as seen in the TG curve, is 90% and fully corresponds to the exothermic effect on the DSC curve. The UBH STA curve (II) shows that this raw material is less thermally stable. The endo-effect is already visible at $111.9^\circ C$, which can be explained by the evaporation of the moisture. In the TG curve, this effect corresponds to a small (8%) mass loss. The DSC curve shows much smaller and larger exo-effects in the temperature range of 409.5 – $529.4^\circ C$ that represent the combustion processes of various organic substances. This range corresponds to a total mass loss of 16.44%. Such relatively small mass loss indicates that not all organic matter present in the UBH burns in the temperature range studied.

Based on the analysis and evaluation of the results of chemical and instrumental analysis, it can be stated that both wastes from the production of the buckwheat groats are suitable for the production of environmentally friendly bulk fertilizers.

3.2. Granulation of the Buckwheat Husk Ash and Uncleaned Buckwheat Husks

In JSC “Ekofrisa”, about 23% of the buckwheat husks are produced during the seed production process. Furthermore, about 2% of ash results after burning these husks. Typically, obtained husk ash is very fine—less than 1 mm—and is separated and collected from the gas stream in a cyclone. The direct use of this ash is problematic, since an efficient and even distribution of it on soil is very difficult; therefore, in order to perform compacting or granulation, it is necessary to improve storage, transportation and application into the soil.

Our preliminary experiments using dilute H_3PO_4 as a binding agent, as well as literature data [28,29], have shown that bioderived ash granulation without designated binders results in poor quality granules. Starch-g-polyvinyl acetate (PVA) has previously been prepared by the graft copolymerization of starch with vinyl acetate to yield slow-release urea fertilizers [30]. Other polymers have also been used [31], including polycaprolactone or polyacrylamide [32], poly (butylene succinate) and butylene ester of dilinoleic acid [33] and sodium alginate [34], to name a few, in a recent development to yield enhanced efficiency urea and NPK [31,35] fertilizers via the (bio)polymer coating tailoring release pattern of the nutrients to closely match the growth requirement of the plants. All in all, we used this knowledge and an implicit binding property of PVA. In our experiments, 10% solution of PVA was used as a binder to produce granules of BHA or BHA and UBH mixture. Thirty-one granulation experiments (repeated three times) were performed for BHA and UBH granulation.

3.3. The Properties of the Granular Buckwheat Husks Ash and Uncleaned Buckwheat Husks Fertilizers

The objective function of these granulation experiments was to select the optimal composition of the raw materials to obtain fertilizers of suitable quality. Therefore, the key properties of all samples, including granule fractional size, moisture content, crushing strength, loose bulk density, as well as pH of 10% solution, were measured and are shown in Table 2 and Figures 4–6.

Table 2. Properties of BHA and UBH granules.

Sample No.	Raw Materials Humidity, %	Granules Size Distribution, %						pH of 10% Solution	Granule Crushing Strength, N/gran.
		>5 mm	4–5 mm	3.15–4 mm	2–3.15 mm	1–2 mm	<1 mm		
100% BHA									
1	41.2	8.9 ± 0.14	1.5 ± 0.14	4.1 ± 0.14	2.7 ± 0.25	44.7 ± 0.29	38.1 ± 0.29	12.0 ± 0.38	6.30 ± 0.19
2	44.4	2.2 ± 0.38	3.4 ± 0.87	3.9 ± 0.52	7.1 ± 0.52	35.3 ± 0.89	48.1 ± 0.63	12.0 ± 0.87	6.18 ± 0.42
3	47.4	10.1 ± 0.87	6.8 ± 0.66	9.6 ± 0.49	10.4 ± 0.63	18.8 ± 0.38	44.3 ± 0.49	11.5 ± 0.76	6.36 ± 0.32
4	50.0	16.6 ± 0.76	8.1 ± 0.25	10.3 ± 0.19	12.4 ± 0.52	21.9 ± 0.38	30.7 ± 0.63	11.5 ± 0.25	6.47 ± 0.21
5	52.4	10.0 ± 0.31	11.9 ± 0.14	7.1 ± 0.56	19.3 ± 0.38	39.2 ± 0.38	12.5 ± 0.25	12.0 ± 0.71	6.45 ± 0.11
6	53.5	16.3 ± 0.49	10.8 ± 0.38	16.3 ± 0.52	21.5 ± 0.38	29.7 ± 0.75	5.4 ± 0.14	11.5 ± 0.38	6.82 ± 0.13
7	54.4	37.0 ± 0.76	18.5 ± 0.38	18.4 ± 0.75	16.3 ± 0.29	8.1 ± 0.52	1.7 ± 0.25	11.0 ± 0.45	6.91 ± 0.17
8	55.6	30.6 ± 0.25	20.3 ± 0.63	19.3 ± 0.14	14.0 ± 0.38	12.8 ± 0.38	3.0 ± 0.38	11.5 ± 0.75	7.39 ± 0.41
9	56.5	64.4 ± 0.49	21.6 ± 0.52	7.8 ± 0.38	4.4 ± 0.49	1.1 ± 0.25	0.7 ± 0.19	11.0 ± 0.63	6.61 ± 0.25
80% BHA and 20% UBH									
10	23.1	2.6 ± 0.63	2.4 ± 0.14	3.4 ± 0.25	10.3 ± 0.63	27.1 ± 0.38	54.2 ± 0.38	10.5 ± 0.25	Plastic deformation at 6–7 N/gran.
11	28.6	17.5 ± 0.63	7.4 ± 0.38	8.7 ± 0.38	15.4 ± 0.49	29.6 ± 0.87	21.4 ± 0.87	10.5 ± 0.25	
12	31.0	36.4 ± 0.63	13.4 ± 0.38	14.9 ± 0.29	23.1 ± 0.25	7.8 ± 0.52	4.4 ± 0.49	10.5 ± 0.43	
13	33.3	18.0 ± 0.66	13.6 ± 0.49	15.1 ± 0.66	25.5 ± 0.38	16.4 ± 0.25	11.4 ± 0.25	10.5 ± 0.38	
14	35.5	60.6 ± 0.52	16.7 ± 0.43	11.2 ± 0.25	4.7 ± 0.25	1.5 ± 0.38	5.3 ± 0.14	10.0 ± 0.52	
15	37.5	57.9 ± 0.38	16.9 ± 0.89	7.0 ± 0.25	2.8 ± 0.25	4.0 ± 0.38	11.4 ± 0.29	10.0 ± 0.49	
60% BHA and 40% UBH									
16	28.6	1.1 ± 0.38	2.6 ± 0.38	4.8 ± 0.52	10.5 ± 0.52	25.8 ± 0.52	55.2 ± 0.25	10.3 ± 0.49	Plastic deformation at 5–6 N/gran.
17	33	4.4 ± 0.38	7.0 ± 0.49	10.3 ± 0.38	23.8 ± 0.38	32.6 ± 0.25	21.9 ± 0.29	10.3 ± 0.14	
18	37.5	4.9 ± 0.25	8.0 ± 0.49	14.1 ± 0.75	28.7 ± 0.25	24.1 ± 0.52	20.2 ± 0.52	10.3 ± 0.52	
19	39.4	8.1 ± 0.52	13.7 ± 0.38	17.8 ± 0.52	28.4 ± 0.38	16.5 ± 0.49	15.5 ± 0.66	10.0 ± 0.63	
20	41.2	17.8 ± 0.38	16.5 ± 0.14	19.7 ± 0.38	16.9 ± 0.52	8.4 ± 0.38	20.7 ± 0.38	10.1 ± 0.14	
21	42.9	12.9 ± 0.52	16.6 ± 0.29	15.6 ± 0.29	11.9 ± 0.63	9.3 ± 0.63	33.7 ± 0.38	10.0 ± 0.29	
22	44.4	15.1 ± 0.38	15.9 ± 0.25	13.9 ± 0.25	10.7 ± 0.38	9.2 ± 0.25	35.2 ± 0.25	10.0 ± 0.14	
40% BHA and 60% UBH									
23	37.5	0.0 ± 0.52	0.9 ± 0.49	3.1 ± 0.25	14.2 ± 0.38	40.7 ± 0.76	41.1 ± 0.25	10.1 ± 0.14	Plastic deformation at 5–6 N/gran.
24	44.4	4.2 ± 0.25	9.0 ± 0.49	16.1 ± 0.38	25.9 ± 0.63	18.1 ± 0.52	26.7 ± 0.49	10.1 ± 0.14	
25	47.4	12.9 ± 0.49	16.1 ± 0.38	9.7 ± 0.52	29.2 ± 0.49	15.4 ± 0.38	16.7 ± 0.38	10.0 ± 0.25	
26	48.7	10.2 ± 0.38	17.3 ± 0.38	19.3 ± 0.52	22.5 ± 0.49	11.7 ± 0.25	19.0 ± 0.49	10.0 ± 0.29	
27	50.0	7.4 ± 0.38	13.3 ± 0.63	15 ± 0.38	16.2 ± 0.49	12.4 ± 0.38	35.3 ± 0.38	9.9 ± 0.14	
20% BHA and 80% UBH									
28	47.4	9.3 ± 0.38	11.7 ± 0.49	15 ± 0.38	30.8 ± 0.79	19.7 ± 0.38	13.2 ± 0.25	9.9 ± 0.14	Plastic deformation at 5 N/gran.
29	48.7	9.3 ± 0.38	12.2 ± 0.29	15.9 ± 0.66	29.3 ± 0.63	19.3 ± 0.25	14.0 ± 0.52	9.8 ± 0.29	
30	50.0	10.5 ± 0.38	16.6 ± 0.25	15.3 ± 0.38	25.8 ± 0.38	18.1 ± 0.52	13.7 ± 0.25	9.8 ± 0.14	
31	51.2	26.0 ± 0.63	21.4 ± 0.49	18 ± 0.57	20.0 ± 0.63	6.8 ± 0.52	7.8 ± 0.52	9.7 ± 0.29	

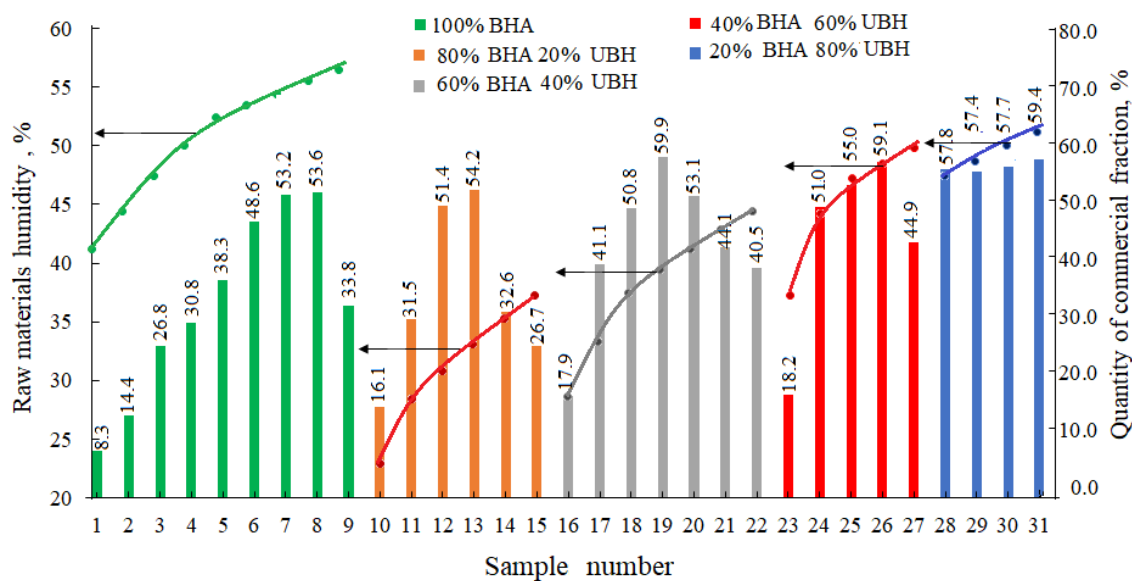


Figure 5. Influence of raw material content and humidity on the commercial fraction of the granular fertilizers.

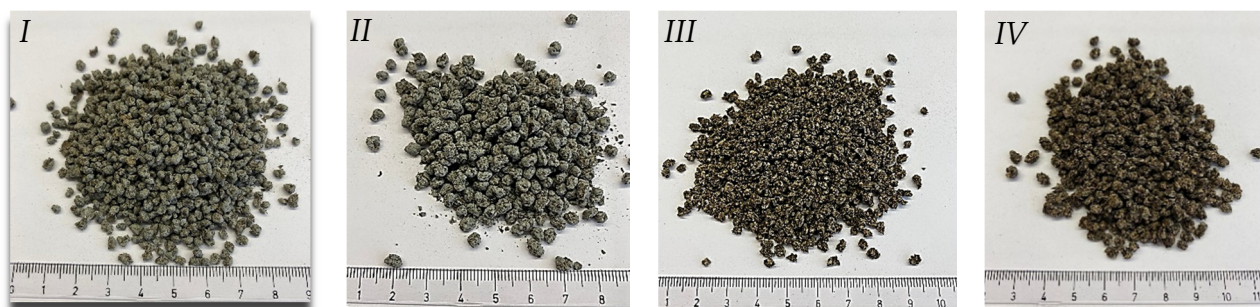


Figure 6. Shape of granules at different ratios of BHA and UBH: (I)—80% BHA and 20% UBH; (II)—60% BHA and 40% UBH; (III)—40% BHA and 60% UBH; IV—20% BHA and 80% UBH.

As seen from the data in Table 2, the mixture of the raw materials with different humidity was prepared depending on the ratio of BHA and UBH. As shown in Figure 5, the granulation of the pure ash (100% BHA) required a maximum of 10% PVA solution (up to 56.5%). Meanwhile, at a ratio of 4:1 = BHA:UBH (80% and 20%), the lowest amount of liquid binder was used (23.1–37.5%). As the amount of UBH in the raw material mixture increased (up to 80%), the need for binder increased as well but still remained lower than in the granulation of the pure ash.

The size distribution of the produced granules depends on the moisture content of the raw material mixture and ranges from less than 1 mm to more than 5 mm. At higher humidity, larger granules are formed regardless of the ratio between BHA and UBH. Since the goal of granulation is to obtain as much commercial fraction (2–5 mm) as possible, these data are analysed in more detail and presented in Figure 5.

It can be seen that the 2–5 mm granule size depends on a certain degree of moisture of the raw materials and on the ratio of BHA and UBH.

Based on the dependencies discussed above (Figure 5), in the samples where ash is dominating (Samples 1–22), the uniform dependence of the commercial fraction on the humidity of the raw materials mixture can be seen. The optimum moisture content of each group with a different ratio of BHA to UBH corresponds to the highest content of the commercial fraction. For example, the highest amount of commercial fraction of 100% BHA granules was obtained in samples 7 and 8 when 53.5–54.4% of PVA solution was added to

the raw material mixture, whereas for the ratio 4:1 = BHA:UBH, to obtain almost the same amount of commercial fraction, only 31.0–33.3% of PVA solution was required. The highest content of the commercial fraction (59.9%) was found in the mixture of raw materials, at 60% BHA, 40% UBH, and 39.4% PVA solution (Sample 19). A less significant effect of raw material moisture was found in samples 23–31 with higher content of UBH. Almost 60% of the commercial fraction was obtained here in a wide range of raw material moisture (44.4%–51.2%). However, it should be noted that the higher the amount of UBH, the more moisture is needed to form the granules. The pH of 10% solution of the produced granules were analysed (Table 2), and data showed that the 10% PVA solution (despite being slightly acidic, pH 3) did not neutralise the high alkalinity of the ash (pH of 10% solution equals 12.5). The pH of the 100% BHA granules ranged from 11.0 to 12.0. After adding 20–80% ground UBH (pH of 10% solution equals 6.5) to BHA, the pH of the 10% fertilizer solution decreased insignificantly and ranged from 10.5 to 11.5. Such pH values of the fertilizer have led to the conclusion that the fertilizer can act as a liming agent and, therefore, can be recommended for the fertilizing of acid soils.

Another important parameter characterizing the bulk fertilizer is the strength of the granules, which was also analysed in this work. However, it should be mentioned that only the ash granules were crushed, and their strength measured (6.18–7.39 N/gran.), despite the fact that they had a rather regular spherical shape (Figure 6).

Other granules were plastic; they did not crush within the measuring range of the device (5–200 N). They only had plastic deformation at 5–7 N/gran. These results correlate with the other scientists' results that were obtained during the production and analysis of the cylindrical granules [36]. Moreover, higher biomass also affects the surface of the granules because the drum granulator without the compression was used. The photos in Figure 6 show that the surface of the granules of the fertilizer, which contains 60% or 80% biomass, is rough, and its colour is dark, but granules are stable and dust-free.

It can be seen that the humidity of 2–5 mm size granules (Figure 7) greatly depends on the composition of the raw material mixture. After drying at 100 °C to the constant weight of the sample, the humidity of the pure ash commercial fraction granules (Sample 1–9) was the lowest (1.7–2.0%). The humidity of the granules containing UBH increases depending on the amount of UBH, and was the highest (8.8–10.5) at a ratio of 1:4 = BHA:UBH. The loose bulk density of BHA was 470.9 kg/m³ and, for UBH, this value was 411.0 kg/m³ (slightly smaller). The addition of PVA solution and humidity of the final granulated product can affect the bulk density of the final product (Figure 7).

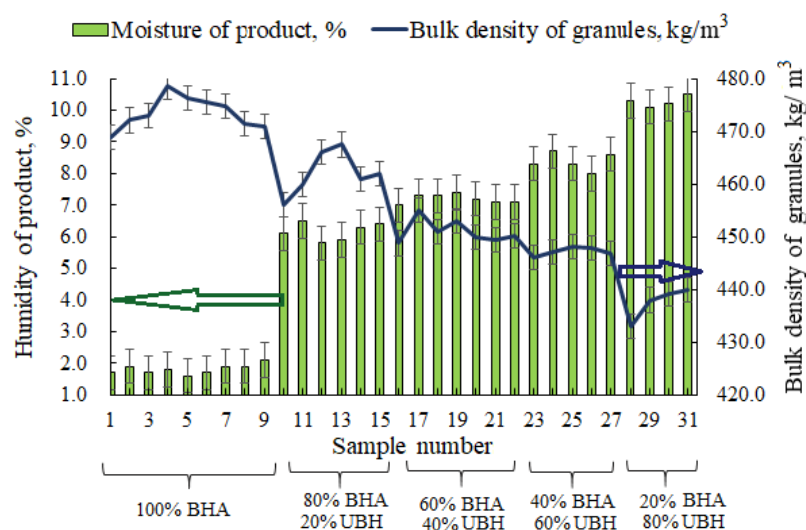


Figure 7. The dependence of the humidity and loose bulk density of granular fertilizers (2–5 mm) on the composition of the raw material mixture.

The loose bulk density varied in a small range from 430 kg/m³ to 470 kg/m³, but it is clear that despite the higher humidity, the density of fertilizer granules with a ratio of 1:4 = BHA:UBH was slightly lower due to their high (80%) UBH content. In summary, when more than 20% of UBH was used in the raw material mixture, the amount of the commercial fraction granules was high (55–59%), but they were of poor quality because of high humidity (more than 6%) and low bulk density (less than 450 kg/m³).

Commercial (2–5 mm size) fractions obtained using different raw material mixtures and 10% PVA solution (sample 12, 19, 26 and 30) were loaded into a desiccator above a saturated NaNO₂ solution and H₂O. All samples were held for 17 days at 21–23 °C and 70–75% or 99–100% relative humidity, respectively. The mass increase was measured and is tabulated in Figure 8.

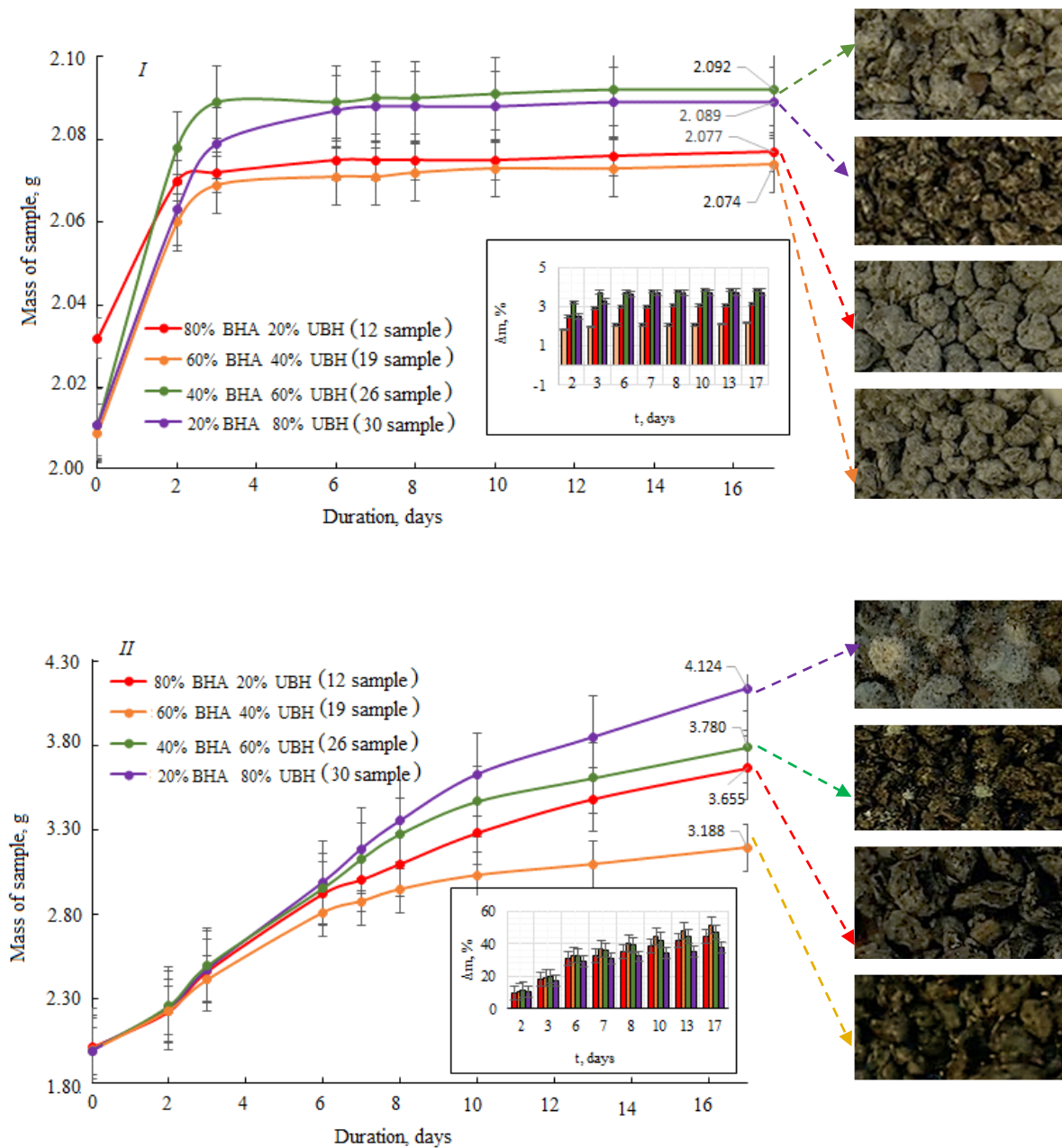


Figure 8. The dependence of the absorbed moisture content of the granular fertilizers (2–5 mm) on the composition of the raw material mixture: (I) in the saturated NaNO₂ solution environment; (II) in an H₂O environment.

Data in Figure 8I show a clear difference in the trend of the absorbed moisture depending on the desiccator environment. In an aqueous NaNO_2 environment, a steady-state saturation of the absorbed moisture content (2–4%) was reached after 6 days.

A slightly higher change in mass was observed in the samples with a higher content of UBH (60% and 80%). However, in general, it can be stated that these samples were non-hygroscopic when stored in the NaNO_2 environment. Importantly, absorption curves of moisture shown in Figure 8I exhibit two different regimes: in the first one, the increase in moisture is large and is followed by no uptake of moisture, and the granules do not lose their shape and properties. Different trend curves are seen in Figure 8II, representing the results of storage in a very humid environment. The largest moisture uptake of 45–50% was observed for samples obtained using 60% and 80% of UBH. However, even after 17 days, the mass of all samples increased, with mold forming on some samples. This means that additional anti-hygroscopic substances should be used while transporting granules like these by sea or during storage in wet surroundings.

In order to evaluate the processes taking place during the production and the stability of the produced fertilizers, the instrumental analysis of the fertilizer (Sample 12) was performed, and the obtained results were compared with the analogous results of the analysis of the raw materials (Figures 2–4). The results of the FT-IR (Figure 2 curve III) and XRDA (Figure 3 curve III) analysis suggest that no chemical reaction took place during the mixing, granulation, and drying processes of the raw materials. The spectra of the fertilizer samples show the same peaks, and the same chemical bonds or chemical compounds can be identified as in the spectra of raw materials. In the FT-IR spectrum (Figure 4 curve III), one new peak in the area of 2400 cm^{-1} can be assigned to the $\text{C}=\text{O}=\text{C}$ bond that is characteristic of the binder PVA used in the granulation process. It can be seen that some peaks are more intense, but BHA-specific peaks predominate, and this correlates with the composition of the raw materials (12 samples contain 80% BHA and 20% UBH). Another situation has been revealed by the analysis of thermal stability (STA) data. Here, the DSC curve shows that the fertilizer sample, like UBH, has an endothermic effect at $90.9\text{--}135.6\text{ }^\circ\text{C}$ and the moisture removal also took place, which is indicated by a small mass loss (TG curve). At higher temperatures of $343.8\text{--}650.5\text{ }^\circ\text{C}$, the exothermic effects are similar to those in the UBH DSC curve and occurred due to the combustion of the organic substances.

4. Conclusions

Based on the results of the chemical and instrumental analysis, it can be stated that both wastes from the production of the buckwheat groats can be used for the production of environmentally friendly bulk fertilizers. Using a drum granulator, the highest content of the commercial fraction (up to about 60%) was produced from the mixture of raw materials with compositions of 60–20% BHA, 40–80% UBH, and 47–50% PVA (10% solution). However, when more than 20% of the UBH were used in the raw materials mixture, granules had a high humidity (more than 6%) and a low bulk density (less than 450 kg/m^3). The pH values of 10% solution of the produced granules ranged from 12.0 to 9.7, indicating that the fertilizers can act as a liming agent, which is recommended while fertilizing acid soils. It should also be mentioned that only ash granules were crushed and their strength measured ($6.18\text{--}7.39\text{ N/gran.}$), whereas other granules had plastic deformations at $5\text{--}7\text{ N/gran.}$ Granulated fertilizers are non-hygroscopic when stored at $21\text{--}23\text{ }^\circ\text{C}$ and 70–75% humidity and keep their shape. The analysis data suggest that no chemical reaction took place during the mixing, granulation, and drying processes of the raw materials, and the same peaks in FT-IR and XRDA spectra of the produced fertilizers indicate the presence of the same chemical bonds or chemical compounds as in the raw materials.

In summary, the waste from buckwheat groats can be used in the production of environmentally friendly fertilizers to reduce environmental pollution, slow down soil degradation, and increase soil organic matter.

Author Contributions: Conceptualization, R.Š.; methodology, O.P.; formal analysis, O.P.; data curation, O.P. and R.Š.; writing—original draft preparation, O.P. and R.Š.; writing—review and editing, R.Š. and O.P.; visualization, O.P. and R.Š.; supervision, R.Š. All authors have read and agreed to the published version of the manuscript.

Funding: This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Sharing the data presented in this study is not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Wijngaard, H.H.; Arendt, E.K. Buckwheat. *Cereal Chem. J.* **2006**, *83*, 391–401. [CrossRef]
2. Pomeranz, Y.; Lorenz, K. Buckwheat: Structure, composition, and utilization. *Crit. Rev. Food Sci. Nutr.* **1983**, *19*, 213–258. [CrossRef] [PubMed]
3. Kayashita, J.; Shimaoka, I.; Nakajoh, M.; Yamazaki, M.; Kato, N. Consumption of Buckwheat Protein Lowers Plasma Cholesterol and Raises Fecal Neutral Sterols in Cholesterol-Fed Rats Because of Its Low Digestibility. *J. Nutr.* **1997**, *127*, 1395–1400. [CrossRef] [PubMed]
4. Tolaini, V.; Del Fiore, A.; Nobili, C.; Presenti, O.; De Rossi, P.; Procacci, S.; Vitali, F.; Brunori, A. Exploitation of Tartary Buckwheat as Sustainable Ingredient for Healthy Foods Production. *Agric. Agric. Sci. Procedia* **2016**, *8*, 455–460. [CrossRef]
5. Khanh, T.D.; Chung, M.I.; Xuan, T.D.; Tawata, S. The Exploitation of Crop Allelopathy in Sustainable Agricultural Production. *J. Agron. Crop Sci.* **2005**, *191*, 172–184. [CrossRef]
6. Corporate Statistical Database (FAOSTAT). Buckwheat Production in 2019, Crops/Regions/World list/Production Quantity (Pick Lists). Available online: <https://www.fao.org/faostat/en/#data/QCL> (accessed on 28 January 2022).
7. Kojima, Y.; Obara, Y. Utilization of Buckwheat Husks through a Two-stage Cooking and Carbonization Treatment. *J. Jpn. Soc. Waste Manag. Expert* **2007**, *18*, 137–144. [CrossRef]
8. Wronkowska, M.; Haros, M. Wet-milling of buckwheat with hull and dehulled—The properties of the obtained starch fraction. *J. Cereal Sci.* **2014**, *60*, 477–483. [CrossRef]
9. Zielinska, D.; Szawara-Nowak, D.; Zielinski, H. Antioxidative and Anti-Glycation Activity of Buckwheat Hull Tea Infusion. *Int. J. Food Prop.* **2013**, *16*, 228–239. [CrossRef]
10. Whittaker, C.; Borrión, A.L.; Newnes, L.; McManus, M. The renewable energy directive and cereal residues. *Appl. Energy* **2014**, *122*, 207–215. [CrossRef]
11. Foo, K.Y.; Hameed, B.H. Utilization of rice husk ash as novel adsorbent: A judicious recycling of the colloidal agricultural waste. *Adv. Colloid Interface Sci.* **2009**, *152*, 39–47. [CrossRef]
12. McDonough, W.; Braungart, M. *Cover of Cradle to Cradle: Remaking the Way We Make Things*; North Point Press: New York, NY, USA, 2002.
13. Zhang, H.; Frey, M.; Navizaga, C.; Lenzo, C.; Taborda, J.; Taifan, W.; Sadeghnejad, A.; Sviklas, A.M.; Baltrusaitis, J. Dairy Wastewater for Production of Chelated biodegradable Zn Micronutrient Fertilizers. *ACS Sustain. Chem. Eng.* **2016**, *4*, 1722–1727. [CrossRef]
14. Chemical Book. Available online: https://www.chemicalbook.com/ProductChemicalPropertiesCB3700594_EN.htm (accessed on 17 September 2021).
15. Schumacher, B.A. Methods for the determination of total organic carbon (TOC) in soils and sediments. *Ecol. Risk Assess Support Cent.* **2002**, 1–23.
16. Fulton, J. Physical Properties of Granular Fertilizers and Impact on Spreading. CFAES. 2016. Available online: <https://ohioline.osu.edu/factsheet/fabe-5501> (accessed on 4 October 2021).
17. Lazdovica, K.; Kampars, V.; Liepina, L.; Vilka, M. Comparative study on thermal pyrolysis of buckwheat and wheatstraws by using TGA-FTIR and Py-GC/MS methods. *J. Anal. Appl. Pyrolysis* **2017**, *124*, 1–15. [CrossRef]
18. Mudunkotuwa, I.A.; Minshid, A.A.; Grassian, V.H. ATR-FTIR spectroscopy as a tool to probe surface adsorption on nanoparticles at the liquid–solid interface in environmentally and biologically relevant media. *Analyst* **2014**, *139*, 870–881. [CrossRef] [PubMed]
19. Brian, C.S. *Fourier Transform Infrared Spectroscopy*; CRC Press Taylor & Francis Group: Darmstadt, Germany, 2011; p. 193.
20. Hummel, D. *Atlas of Plastics additives. Analysis by Spectrometric Methods*; Springer: Berlin/Heidelberg, Germany, 2002; p. 537.
21. Baltrusaitis, J.; Schuttlefield, J.; Zeitler, E.; Grassian, V.H. Carbon dioxide adsorption on oxide nanoparticle surfaces. *Chem. Eng. J.* **2011**, *170*, 471–481. [CrossRef]
22. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B: Applications in Coordination, Organometallic, and Bioinorganic Chemistry*; John Wiley & Sons: Hoboken, NJ, USA, 2009; ISBN 9780470405840.

23. Vaickelionis, G.; Valančienė, V. Lightweight Concrete with an Agricultural Waste—Buckwheat Husk. *Mater. Sci.* **2016**, *22*, 98–104. [[CrossRef](#)]
24. Peys, A.; Mobili, A.; Arnout, L.; Rahier, H.; Blanpain, B.; Pontikes, Y. One-part inorganic polymers from residues only: Biomass ash activation of Fe-rich slag. In Proceedings of the 5th International Conference on Industrial and Hazardous Waste Management, Chania, Greece, 27–30 September 2016; ISBN 978-960-8475-24-3.
25. Vaiciukynienė-Palubinskaitė, D.; Nizevičienė, D.; Kantautas, A.; Bocullo, V.; Kiele, A. Alkali Activated Paste and Concrete Based on of Biomass Bottom Ash with Phosphogypsum. *Appl. Sci.* **2020**, *10*, 5190. [[CrossRef](#)]
26. Baek, C.; Junhyung, S.; Choi, M.; Cho, J.; Ahn, J.; Cho, K. Utilization of CFBC Fly Ash as a Binder to Produce In-Furnace Desulfurization Sorbent. *Sustainability* **2018**, *10*, 4854. [[CrossRef](#)]
27. Lai, L.W.; Ibrahim, M.; Rahim, N.M.; Hashim, E.F.; Ya'cob, M.Z.; Idris, A.; Akhtar, J. Study on composition, structural and property changes of oil palm frond biomass under different pretreatments. *Cellulose Chem. Technol.* **2016**, *50*, 951–959.
28. Demeyer, A.; Voundi Nkana, J.C.; Verloo, M.G. Characteristics of wood ash and influence on soil properties and nutrient uptake: An overview. *Bioresour. Technol.* **2001**, *77*, 287–295. [[CrossRef](#)]
29. Paleckienė, R.; Sviklas, A.M.; Slinksienė, R.; Streimikis, V. Processing of rape straw ash into compound fertilizers using sugar factory waste. *Polish J. Environ. Stud.* **2012**, *21*, 993–999.
30. Niu, Y.; Li, H. Controlled Release of Urea Encapsulated by Starch-g-poly(vinyl acetate). *Ind. Eng. Chem. Res.* **2012**, *51*, 12173–12177. [[CrossRef](#)]
31. Timilsena, Y.P.; Adhikari, R.; Casey, P.; Muster, T.; Gill, H.; Adhikari, B. Enhanced efficiency fertilisers: A review of formulation and nutrient release patterns. *J. Sci. Food Agric.* **2015**, *95*, 1131–1142. [[CrossRef](#)] [[PubMed](#)]
32. Pereira, E.I.; da Cruz, C.C.T.; Solomon, A.; Le, A.; Cavigelli, M.A.; Ribeiro, C. Novel Slow-Release Nanocomposite Nitrogen Fertilizers: The Impact of Polymers on Nanocomposite Properties and Function. *Ind. Eng. Chem. Res.* **2015**, *54*, 3717–3725. [[CrossRef](#)]
33. Lubkowski, K.; Smorowska, A.; Grzmil, B.; Kozłowska, A. Controlled-Release Fertilizer Prepared Using a Biodegradable Aliphatic Copolyester of Poly(butylene succinate) and Dimerized Fatty Acid. *J. Agric. Food Chem.* **2015**, *63*, 2597–2605. [[CrossRef](#)]
34. Schneider Teixeira, A.; Deladino, L.; Zaritzky, N. Yerba Mate (*Ilex paraguariensis*) Waste and Alginate as a Matrix for the Encapsulation of N Fertilizer. *ACS Sustain. Chem. Eng.* **2016**, *4*, 2449–2458. [[CrossRef](#)]
35. Du, C.; Zhou, J.; Shaviv, A. Release Characteristics of Nutrients from Polymer-coated Compound Controlled Release Fertilizers. *J. Polym. Environ.* **2006**, *14*, 223–230. [[CrossRef](#)]
36. Frodeson, S.; Lindén, P.; Henriksson, G.; Berghel, J. Compression of Biomass Substances—A Study on Springback Effects and Color Formation in Pellet Manufacture. *Appl. Sci.* **2019**, *9*, 4302. [[CrossRef](#)]