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PHYSICAL-CHEMICAL CHARACTERIZATION OF INDUSTRIAL WASTE FROM SUNFLOWER HUSK COMBUSTION FOR POTENTIAL GREEN APPLICATIONS

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ABSTRACT

The industrial ash used in this study is a residue from the combustion of plant biomass - sunflower husks. The increasing generation of this type of waste and the need for implementation of sustainable practices warrant the investigation of its possible green applications.

The study presents the results on the chemical and phase composition of two series of fly ash samples obtained from the industrial combustion of sunflower husks using wavelength-dispersive X - ray fluorescence analysis, powder X - ray diffraction, and Fourier transform infrared spectroscopy. The chemical data of the samples show high contents of biogenic and nutritional oxides such as K (34 - 39 % wt.), S (5 - 11 % wt.), and Ca (3 - 8 % wt.), with no detectable contamination with toxic or radioactive elements. The phase composition of the samples includes synthetic analogues of arcanite, K_2CO_3, sylvite, calcite, spurrite, and gypsum. The data obtained demonstrate that this waste material has high potential for use in the production of fertilizer components, activators, or improvers for soils and soil fertility.

Keywords: *sunflower husk, biomass ash, ecology, circular economy.*

INTRODUCTION

In recent decades, the advancement of industries has led to a systematic rise in waste production. The implementation of the circular economy model has necessitated the reconsideration of such waste and its reuse into valuable resources [1]. For example, wastes from coal power plants including bottom ash, slag and fly ash with relatively constant properties and chemical composition have been used successfully in the production of construction materials [2]. The development of alternative energy sources such as biofuels has given rise to the generation of a new type of waste, occurring from the combustion of the biomass in the form of ash. However, this ash currently has little practical use due to its very diverse and inconsistent composition and properties that vary depending on the biomass type burned [3]. Nevertheless, the increasing generation of this type of waste and the need for implementation of sustainable practices warrant the investigation of its possible green applications. Currently, the studies are focused on the application of such ash as a soil improver [4 - 7], as an additive for reducing the boron content in industrial silicon [8], as a component or alternative substitute for coal fly ash in concrete production [9 - 12], and as an additive in biowaste composting [13, 14].

The industrial ash used in this study is a residue from the combustion of plant biomass - sunflower husks. According to preliminary data, it is characterized by a higher content of potassium, phosphorus, and calcium than other plant biomass ashes [3]. It has potential applications in the production of building materials [15, 16]. The content of important biogenic elements suggests the use of sunflower husk ash for organic farming purposes, provided that the composition is proven to be stable and free of contamination with heavy or radioactive elements.

Based on the above-stated observations, the objective of this work is the physical-chemical characterization of sunflower husks fly ash (FA), obtained from a biodiesel production facility in the region of Ruse, Bulgaria. The goal is to characterize two different series of the FA samples, produced at different periods of time to determine their composition, properties, and alteration during weathering. This in turn would allow for further research regarding its possible applications in material sciences. The ash samples were analysed by wavelength-dispersive X - ray fluorescence analysis (WD - XRF), Powder X - ray diffraction (PXRD), and Fourier transform infrared spectroscopy (FT - IR).

EXPERIMENTAL

Materials

Six samples of biomass fly ash produced from the industrial combustion of sunflower shells were analysed for the purposes of this study. The fly ash was produced via grate combustion of sunflower shells cake in a boiler producing water steam. It was collected from a bag cyclone filter at the biodiesel plant of the company Astra Bioplant EOOD, situated in Slivo Pole, Ruse region, Bulgaria. Two series of FA samples were investigated, the first fly ash batch was produced in August 2024 (samples FA - Ia, FA - Ib, FA - Ic) - after exposure to atmospheric conditions, while the second was produced in August 2025 (samples FA - IIa, FA - IIb, FA - IIc) - immediately after receiving the fly ash after the electrostatic precipitator of the plant for the combustion of plant biomass without air retention.

Methods

WD - XRF was used for semi-quantitative analysis of the chemical composition of the samples. Spectrometer WD - XRF Supermini 200 (Rigaku, Japan) was utilized under the following conditions: 50 kV and 4 mA, 200 W X - ray tube with Pd -a node, 30 mm^2 in a helium atmosphere. Depending on the wavelength range, three analysing crystals were used: LIF 200 (for Ti - U), PET (for Al - Ti) and RX25 (for F - Mg). Data processing was performed with the ZSX software package. During the measurements, the lower limit of detection (LLD - Det. Limit) values were determined using the formula Eq. (1):

$$LLD = \frac{3}{S} \cdot \sqrt{\frac{R_b}{t}} \tag{1}$$

where S - sensitivity (cps ppm^{-1}) - sensitivity of the instrument for the specific element (slope of the calibration curve, expressed in pulses per second per unit of concentration, e.g. cps ppm^{-1}); R_b - Background count rate intensity near the peak of the element (cps); t - measurement time (s).

PXRD was applied for the phase identification. The diffraction patterns of the samples were recorded at room temperature using an Empyrean diffractometer (Malvern Panalytical, The Netherlands) equipped with a PIXcel3D detector. Measurements were carried out with Cu Kα radiation (λ = 1.5406 Å) operated at 40 kV and 30 mA, in the 2 θ range of 2 - 70°, with a step size of 0.013° and a counting time of 80 s per step. Diffractograms were evaluated using the Rietveld refinement program Profex, v.5.6.0 [17].

FT - IR spectra were taken using a Bruker Tensor 37 spectrometer (Bruker, Germany) in the spectral range 4000 - 400 cm^{-1}, resolution 1.928 cm^{-1} (100 scans for each sample). The samples were tableted with KBr (0.5 - 1.0 % sample).

RESULTS AND DISCUSSION

Wavelength-dispersive X - ray fluorescence

The XRF data of the two series of FA samples are presented in Table 1. The results of the elemental composition are presented without normalization to the sum of 100 %. The detection limits for the determination of each of the chemical elements present in the composition of the samples are also indicated.

The results reveal that K, Ca, S, Cl are considered major chemical elements, while P, Mg, Si, and Fe are minor elements. No heavy or radioactive metals were detected. This data is important for the potential use of ash from the combustion of this biomass for bio-

Table 1. Elemental composition (wt %) of the two series of fly ash - FA - Ia - c and FA - IIa - c from the combustion of sunflower husks determined by XRF analysis.

Component	Series I						Series II					
	FA -Ia, wt. %	Det. limit	FA -Ib, wt .%	Det. limit	FA - Ic, wt. %	Det. limit	FA -IIa, wt. %	Det. limit	FA -IIb, wt. %	Det. limit	FA -IIc, wt. %	Det. limit
K	34.28	0.01763	34.43	0.02153	36.17	0.01747	36.03	0.02064	39.36	0.02081	38.18	0.02095
S	8.04	0.00915	8.89	0.01011	5.61	0.00782	10.88	0.01008	11.69	0.00916	11.16	0.01042
Ca	8.03	0.03079	7.86	0.03280	6.61	0.02873	4.21	0.03323	3.81	0.03450	3.83	0.03313
Cl	2.40	0.00284	2.38	0.00312	1.66	0.00245	2.26	0.00299	2.67	0.00311	4.46	0.00310
Mg	2.26	0.03473	1.55	0.03438	0.37	0.01660	1.02	0.03328	1.12	0.03251	1.05	0.00800
P	1.18	0.00855	1.04	0.00914	0.58	0.00711	0.37	0.00810	0.39	0.00808	0.37	0.00877
Si	0.15	0.00833	0.14	0.00909	0.07	0.00773	0.06	0.00740	0.05	0.00916	0.05	0.00857
Fe	0.06	0.00637	0.05	0.00839	0.08	0.00637	0.02	0.00763	0.03	0.00804	0.03	0.00707

agricultural purposes. The highest content reveals K, which in the first series of samples is in the range of 34 - 36 %, and in the second series - 36 - 39 %. These high values of K are very perspective for bio-agricultural application because this element is one of the three main nutrients for plants, along with phosphorus and nitrogen. The second most abundant nutritious element is S. It is the fourth most important nutrient for plant nutrition. Its content varies between 5 - 8 % in FA - I and slightly higher, but with minor deviations in FA - II - 10 - 11 %. Hence, K and S in FA - II are present in larger quantities than in FA - I. This difference is probably related to subsequent weathering processes such as hydration and carbonization of FA from series I. The ash from FA - I remained outdoors for several months, including until late autumn 2024, and exposed to atmospheric conditions. In contrast, the ash from series FA - II was obtained immediately after the biomass combustion and collected by the cleaning equipment in the power plant without exposure to weathering. The next most important element is the biogenic Ca (FA - I - 6 - 8 %; FA - II - 3 - 4 %). The amount of Ca is approximately 2 times less in FA - II, nevertheless it is the third element with the highest content in the ash. Although in small quantities, the presence of P (~1 % in FA - I and 0.3 - 0.4 % in FA - II) has also important role in the ash. The insignificant deviations in the contents of elements in the ashes can again be explained by the influence of weathering.

PXRD with Rietveld refinement

When identifying the mineral composition of the samples from series I and II, it was found that their composition is characterized by the occurrence of synthetic analogues of arcanite K_2SO_4, sylvite KCl, gypsum $CaSO_4{\times}2H_2O$, and K_2CO_3 carbonate (Fig. 1a, 1b, 2a, 2b).

More detailed information was obtained from the results of powder X - ray phase analyses with Rietveld refinement performed at (Chi-squared) factor $\chi^2 = 1.79$ (FA - Ia) and $\chi^2 = 1.94$ (FA - IIb) (Fig. 2a and 2b). The results from the PXRD processing are present the main mineral phases in FA and their content in Table 2.

In addition to the main phases - arcanite, K_2CO_3 sylvite, and gypsum - identified by PXRD, the Rietveld refinement supplements the phase composition with calcite, spurrite, and oxides of CaO (in FA - II) and

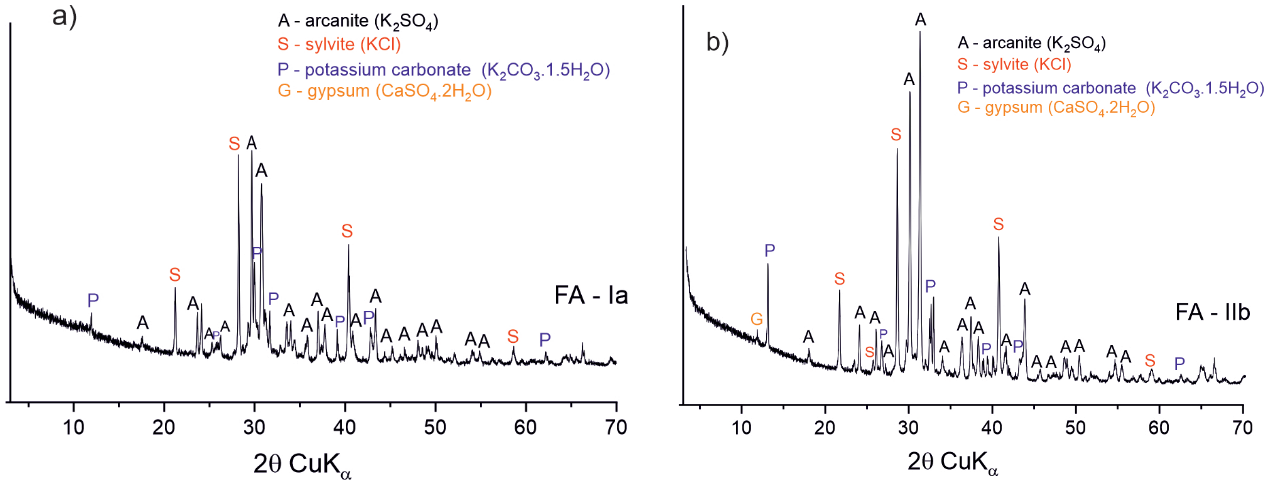

Fig. 1. PXRD patterns of fly ash samples from: (a) series FA - Ia and (b) series FA - IIb.

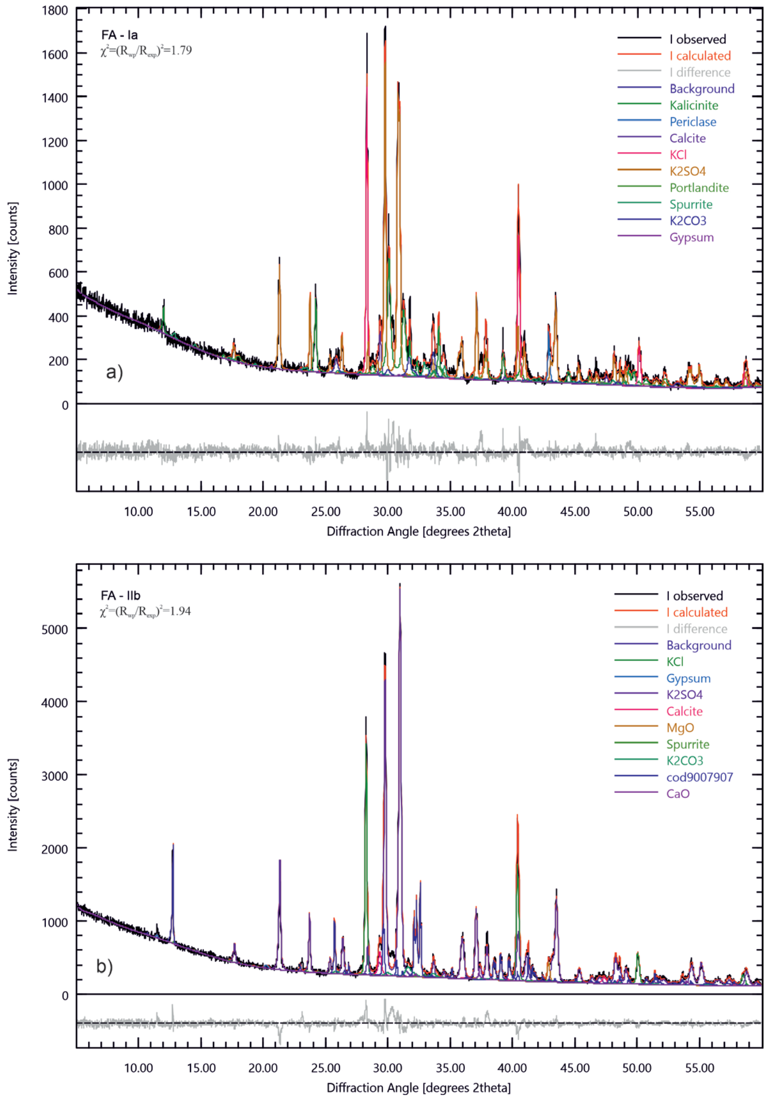

Fig. 2. PXRD patterns with Rietveld refinement of fly ash samples from: (a) series FA - Ia and (b) series FA - IIb.

MgO. It is likely that part of the CaO is transformed into $Ca(OH)_2$ under the influence of moisture in the atmospheric air. In addition to the above-mentioned minerals, another K phase has been identified in the first series - kalicinite ($KHCO_3$) with a high content of about 25 %. Kalicinite is absent from the phase composition of FA - II.

This bicarbonate mineral was probably generated from the transformation of $K_2CO_3 \times 1.5H_2O$ under the influence of moisture and CO_2 in the air and temperature conditions during prolonged storage and weathering. Hence, this FA originated from renewable biomass with net zero CO_2 emissions has an extra capture potential of atmospheric of CO_2. Finally, as a result of biomass combustion in time, waste with a relatively constant composition is formed, containing a high percentage of K sulfate, carbonate, and chloride salts - as well as small amounts of calcite, gypsum, periclase, and lime.

FT - IR spectroscopy

The results of the spectra obtained from average ash samples from series I and II are presented in Fig. 3a, b and Table 3. The spectra show the vibrational modes of the sulfate, carbonate, and hydroxyl anions and the weak and overlapping vibrations of the SiO_4^{4-} group.

The most intense bands in the absorption spectra of

Table 2. Results of Rietveld refinement for fly ash samples from series FA - Ia and series FA - IIb.

No	Phase	Content of phase in FA - Ia, %	Content of phase in FA - IIb, %
1	Arcanite, K_2SO_4	46.06	60.66
2	Sylvite, KCl	8.17	8.70
3	K_2CO_3	5.17	-
4	$K_2CO_3 \times 1.5H_2O$	-	19.51
5	Kalicinite, $KHCO_3$	24.71	-
6	Calcite, $CaCO_3$	2.53	3.42
7	Spurrite, $Ca_5(SiO_4)_2(CO_3)$	6.99	1.05
8	Gypsum, $CaSO_4 \times 2H_2O$	0.24	0.57
9	Periclase, MgO	3.40	1.88
10	Portlandite, $Ca(OH)_2$	2.59	-
11	Lime, CaO	-	0.86

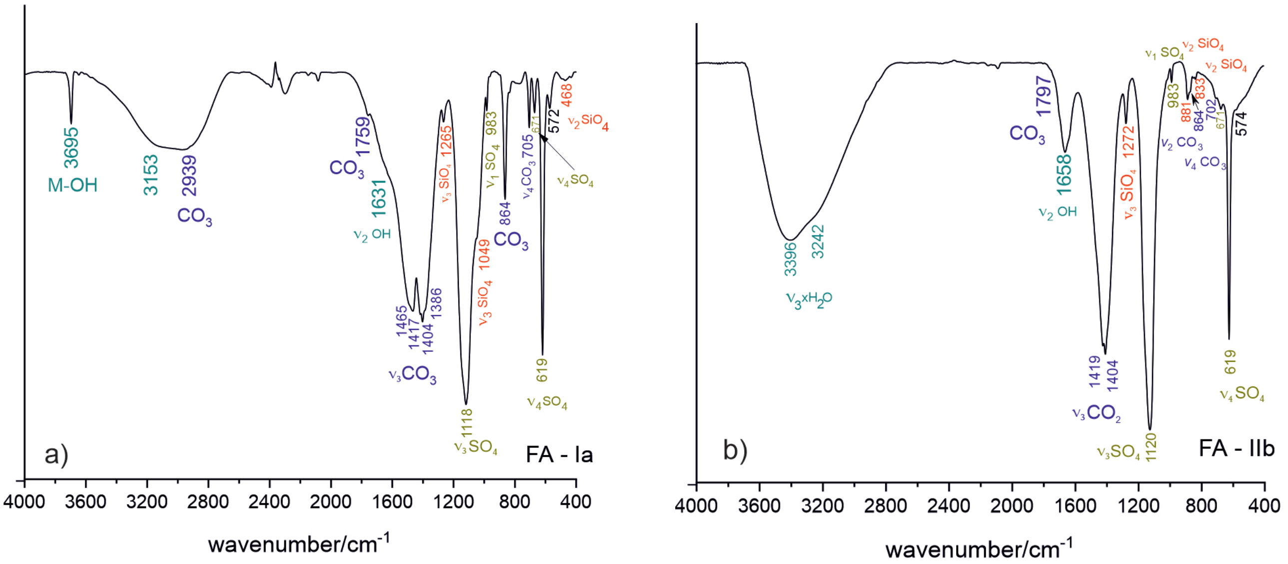

Fig. 3. FT - IR spectra of fly ash samples from: (a) series FA - Ia and (b) series FA - IIb.

Table 3. FT - IR spectroscopy results of samples from: a) FA-I and b) FA-II.

No	Description	Bond	$\mathbf{\nu}_1$, cm^{-1}	$\mathbf{\nu}_2$, cm^{-1}	$\mathbf{\nu}_3$, cm^{-1}	$\mathbf{\nu}_4$, cm^{-1}	Samples	Ref.
1	SO_4^{2-} in K_2SO_4	S-O	983	-	1118	671	FA-I	[18 - 20]
			983	-	1120	671	FA-II	
2	CO_3^{2-} in K_2CO_3 and $Ca_5(SiO_4)_2(CO_3)$	C=O	-	864	1386, 1404, 1417, 1465	705	FA-I	[19 - 21]
			-	864	1404, 1419	702	FA-II	
		C=O $\nu_1 + \nu_4$	-	-	-	1759	FA-I	
			-	-	-	1797	FA-II	
3	SiO_4^{4-} in $Ca_5(SiO_4)_2(CO_3)$	Si-O	-	-	1049, 1265	468	FA-I	[18 - 20]
			-	833, 881	1272	-	FA-II	
4	O-H$^-$ cryst.*	O-H	-	1631	3145	-	FA-I	[22]
				1658	3242, 3396	-	FA-II	
5	O-H^{-} **	M-OH			3695	-	FA-I	[18, 22]
					3696		FA-II	

**O-H crystal. - O-H bond belonging to crystal-bonded water molecules [22].*
***O-H - O-H strongly bound - structurally bound water [22].*

series I and II are observed in the regions of valence and deformation vibrations of the sulfate (at 1118 cm^{-1} and 620 cm^{-1}) and carbonate groups (1380 - 1470 cm^{-1}; 830 - 870 cm^{-1}). This is due to the predominant presence of sulfate and carbonate phases in the samples. In addition, lower intensity vibration bands at 670 and 980 cm^{-1} are also recorded, complementing the spectrum of the sulfate group, and the bands at ~705 cm^{-1} complement the spectrum of the carbonate ion.

The band at ~3690 cm^{-1} characterizes the OH ion in coordination with a metal ion - M - OH in the FA - Ia spectrum, confirming the presence of hydroxide(s) in the composition of ash from series I. It is likely that some of the oxide phases were transformed into hydroxides after absorbing water vapor from the air during their stay in the open storage facility, although they are absent in the PXRD patterns. A similar intense peak of the hydroxyl group at ~3690 cm^{-1} in the IR spectrum of series II is absent, which means that hydroxide phases are absent in this sample.

The absorption around ~3400 cm^{-1} is due to water molecules present in the carbonate phase. In general, the peaks in the region of carbonate asymmetric valence vibrations are narrower and more distinct compared to the sample from series I.

CONCLUSIONS

The data from the various analytical methods applied presents results for the composition of ash obtained in two different time periods during the industrial combustion of sunflower husks in a power plant. The results show that the temperature regime used in the furnace for the burning of the plant biomass maintains the phase composition of the fly ash obtained from the electrostatic precipitator. Prolonged exposure to atmospheric conditions leads to a slight increase in hydrogen salts ($KHCO_3$) and carbonization of K_2O and CaO. They also prove a high percentage of important biogenic nutrient elements such as K, S, P, Ca and Mg, without contamination with toxic or radioactive elements. These results establish the high potential of this waste material for use in the production of fertilizer components, activators, or improvers for soils and soil fertility.

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Authors' contributions

V.P., St.V., Ch.V.: substantial contributions to conception and design; V.P., St.V., Ch.V., K.M.: analysis and interpretation of data; K.M., G.V., R.T., S.P., L.Ts.: writing the original draft of the manuscript; V.P., St.V., Ch.V.: review the draft version of the manuscript; K.M., E.S., R.T. given final approval of the version to be published. All authors read and approved the final manuscript. All authors have participated sufficiently in the work and agreed to be accountable for all aspects of the work.

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