

Research article

Chemical and Mineralogical Characterization of Biomass Ashes for Soil Reinforcement and Liner Material

André Studart^{1,2,3*}, Leonardo Marchiori^{1,2,3}, Maria Vitoria Morais^{1,2,3}, António Albuquerque^{1,2,3}, Pedro Gabriel Almeida^{1,3}, and Victor Cavaleiro^{1,3}

¹Department of Civil Engineering and Architecture, University of Beira Interior, Calçada Fonte do Lameiro, 6201-001, Covilhã, Portugal

² FibEnTech, University of Beira Interior, Calçada Fonte do Lameiro, 6201-001, Covilhã, Portugal

³ GeoBioTec, University of Beira Interior, Calçada Fonte do Lameiro, 6201-001, Covilhã, Portugal

Abstract.

Mineralogical and chemical evaluations are necessary to investigate the background and origins of materials. In terms of residues commonly produced around the world, ashes biomass stands out for its high calorific capacity and use for energy production at thermoelectrical facilities. Given current sustainability issues and new demands from society, ashes and soil from pine biomass in the Castelo Branco region were investigated to research possible anthropogenic contaminations, heavy metals among their composition, and their physic-chemical characteristics. These properties can be used to define possible valorisation methods through residue introduction into the soil for its reinforcement and liner application. The results indicated that ashes biomass could help achieve these objectives and could be introduced into the soil, due to its enrichment with pozzolanic minerals and fine granulometry, while having a low-density, which could reduce final weight; however it was considerably different from the original biomass, and contained anthropogenic contaminations and high concentrations of heavy metals.

Keywords: biomass ashes, chemical and mineralogical properties, residue valorisation, soil reinforcement, liner material

1. Introduction

Soils and residues throughout the world can be classified in varied forms, characteristics, and specifications. Based on these properties, investigating their mineralogy can provide background origins and possible anthropogenic contaminations, providing a deeper investigation surrounding the material's origin and its properties. Therefore, fully understanding the background of soils and residues can provide the right tools to understand how to integrate them and ameliorate specific properties, possibly making them successfully applicable to larger applications, such as soft soil reinforcement and liners materials while addressing sustainability issues. Some of these residues, such as biomass ashes, are rich in organic matter gathered from the decomposition of

Corresponding Author: André Studart; email: andre.studart@ubi.pt

Published 10 August 2022

Publishing services provided by Knowledge E

© André Studart et al. This article is distributed under the terms of the [Creative Commons Attribution License](#), which permits unrestricted use and redistribution provided that the original author and source are credited.

Selection and Peer-review under the responsibility of the FibEnTech21 Conference Committee.



vegetables or animals, hence making it feasible for use at thermoelectrical facilities for energy production due to their high calorific value. Although feasible for this activity, these facilities can alter biomass' properties as they suffer burns with temperatures up to 1400°C while being also co-fired with coal [1], which is a highly calorific material that is contaminant itself. Therefore, it is important to investigate anthropogenic contamination on these residues, as they can present contamination properties, which are necessary to be evaluated through X-Ray diffraction (XRD) and X-Ray fluorescence (XRF) tests.

Thus, this paper aims to investigate the chemical and mineralogical backgrounds of a soil sample and biomass ashes, in order to research their background and origins for a possible integration and stabilization of this residue within the analysed soil for soils reinforcement and liners materials.

2. Methods

The biomass ashes (BA) were collected at the industrial park of VALAMB - Grupo Razão, located in Castelo Branco (Portugal). The soil for reinforcement was collected at Castelo Branco (Portugal). Both materials were characterized to evaluate their chemical and mineralogical characteristics, as follows: optimum dry density ($\rho_{d,opt}$) and water content, according to standards [2–4]; energy-dispersive X-ray spectroscopy (EDS) for elemental analysis determination, according to equipment S-2700 Hitachi; and X-ray diffraction (XRD) for mineralogical characterization, according to equipment Phillips Analytical X-Ray B.V.

3. Results and discussion

EDS results are presented in Table 1, while Figure 1 and Figure 2 show XRD results for soil and BA, respectively. Both figures use relative intensity in the y-axis in order to obtain the peaks of the minerals.

TABLE 1: EDS elemental analysis of soil and BA

Concentration levels	Soil	BA	Oxides	Soil	BA
Na ₂ O (%)	0.58	1.22	K ₂ O (%)	4.45	7.08
MgO (%)	2.28	4.24	SO ₃ (%)	-	1.84
Al ₂ O ₃ (%)	27.37	17.82	Fe ₂ O ₃ (%)	8.30	5.80
SiO ₂ (%)	56.09	44.87	TiO ₂ (%)	0.93	0.66
CaO (%)	-	14.80	Cd (ppm)		5.07
As (ppm)	-	33.87	Cu (ppm)		63.43

The analysed soil is characterized by having a silty sand granulometry with a 10.5% clay portion, $\rho_{d,opt}$ of 1.92 g/cm^3 related to an optimum water content of 19.40%, which were obtained through granulometry and proctor standards. Its mineralogical composition is characterized by quartz, muscovite, and kaolinite clay, which are characteristic of the Castelo Branco region, where the soil was collected. This region is characterized by an erosive geological episode that flattened a large portion of this area, consisting of K-feldspars, granites, and schists formations [5]. Non-eroded quartzites crests and granites mineral can be found, providing kaolinite clay matrix, which is also evidenced by the sample's whitish colour.

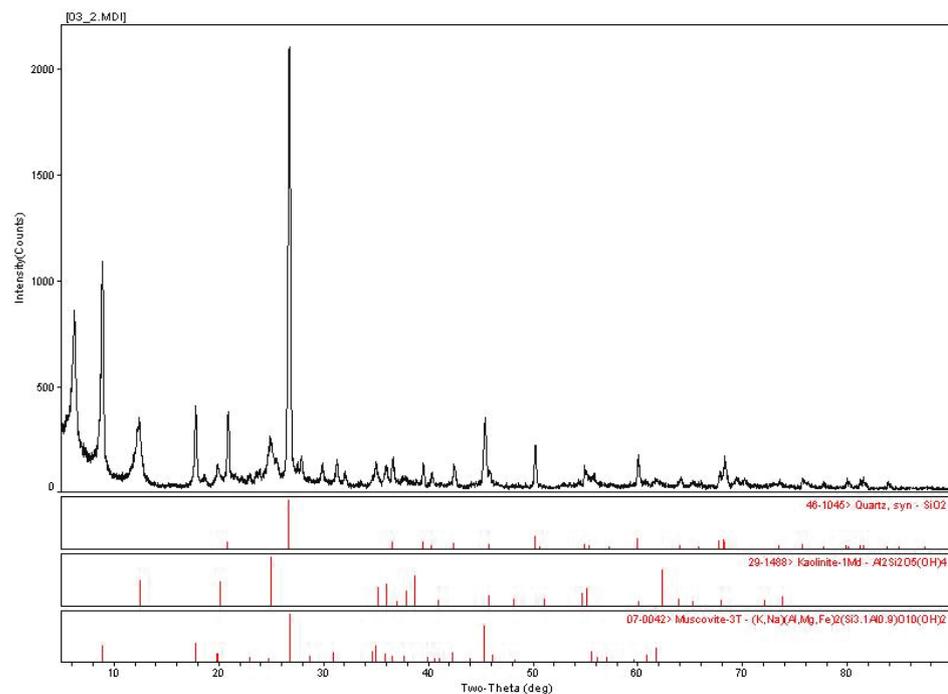


Figure 1: XRD mineralogical characterization of the soil.

The analysed biomass ashes have a finer silty granulometry, proving to be mainly a silty material associated with a $\rho_{d,opt}$ of 1.12 g/cm^3 related to an optimum water content of 25.80%. In addition, it has exposed a heterogenic and highly crystalline composition, which is the result of physical and chemical processes that occur during its combustion, altering BA's structure due to high temperatures - ranging from 500°C up to more than 1000°C - that end up removing most of the organic matter [6]. Quartz, muscovite, orthoclase, and calcite were detected during XRD tests. Quartz is due to the silicious sand used within the biomass combustion process while also typically found, along with the other minerals, in the analysed region. Although the soil provides different minerals to the local vegetation, biomass will also present different composition depending on

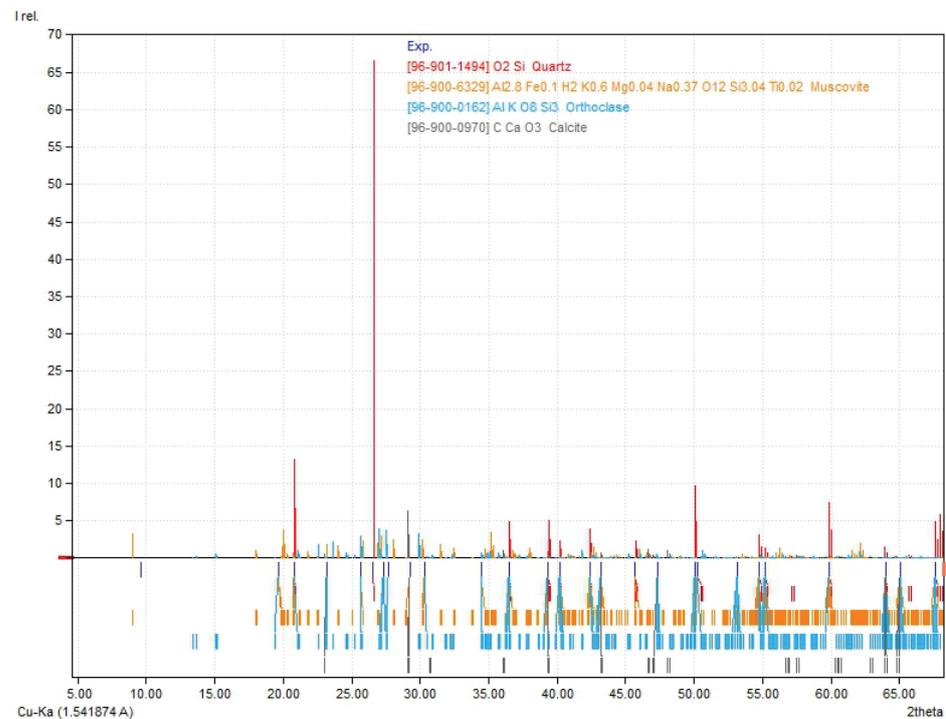


Figure 2: XRD mineralogical characterization of the BA.

the plant species and within different portions of the plant – branches, leaves, or stems – as each one store and concentrate minerals on different levels through different processes [7].

Thus, the used biomass in thermoelectrical facilities is partially understood by the soil and type of vegetation, as it suffers physical-chemical alterations during the combustion due to high temperatures – up to 1400°C - and to the type of used char, which interfere in biomass ashes' composition, deeply altering the original biomass' composition and structure [1]. In addition, during combustion, minerals can suffer enrichment due to thermal-conversions, happening mostly on carbonated minerals [8,9], such as Calcite's (CCaO_3) disintegration to CaO and CO_2 , explaining some high minerals' concentration that is not easily explained by the local soil' chemical composition. Calcium, for example, would be an example of the retaining capacity through oxalate calcium precipitation that plants have, being this element stored in their different portions (branches, trunks, and stems) on different levels, as this is a major element for their development, besides animals' decomposition and bones fragmentation that could also provide calcium concentration for plants [10,11].

When analysing the region where it was first collected, pines are among the most common species in this region, raising suspicion about the biomass' origins. Therefore, the analysed biomass ash is considered here as an aluminosilicate associated with the

original biomass' vegetation – Pines - and to the used char during its combustion. Pines tend to contain high SiO_2 values, and a considerable amount of calcium and aluminium along with accessory elements. In addition, although the exact used char type during the combustion is not known, [12] has shown chars' varied composition, which affects BA composition. All these natural and artificial processes will completely change the final product – BA – compared to the original biomass. As [13,14] have exposed, the belief that biomass itself is sustainable, as it returns to the atmosphere the already used CO_2 value during its incineration, is not fully correct due to these contamination and alteration processes that occur in such facilities, which could lead to a final product that is highly contaminant, as fly ashes are produced in high temperatures up to 1600°C , due to inherent ash particles that retain heavy metals [1,14]. These heavy metals are mostly present due to inherent geological processes that occur during the formation of the above-mentioned minerals. Heavy metals presented in Table 1 on the analysed biomass ashes have shown the materials' susceptibility for contaminating properties, as its Arsenic (As) concentration would not pass Poland's and US New Jersey regulatory limits [15,16] while Cd (Cadmium) concentration would not pass UE's regulatory limits [17]. Thus, this states their contamination potential, although important to reiterate that these values correspond to the full biomass and its introduction in lower percentages into the soil could imply concentrations low enough to attend countries' directives for regulatory limits.

4. Conclusions

Biomass ashes' high variability is a challenge as it is difficult to trace exact patterns due to varied anthropogenic and natural conditions that alter the original biomass, producing new material at the end of the biomass combustion. Apart from this, their granulometry indicates possible soils' void-filling property while its chemical composition shows possible pozzolanic activity due to high Si, Al, and Fe content. Therefore, their background research has indicated anthropogenic contamination plays considerable role in altering biomass' properties and characteristics while also interesting possibilities for soft soils reinforcement due to the above-mentioned properties, although necessary to keep evaluating their contamination potential with leachability tests. Further geomechanical studies are necessary to confirm these characteristics.

Acknowledgments

The authors are grateful to the Foundation for Science and Technology (FCT, Portugal) for financial support by national funds through the projects UIDB/00195/2020 (FibEnTech) and UIDB/04035/2020 (GeoBioTec). The authors are also grateful to João Dias das Neves (VALAMB - Grupo Razão), who provided the samples of biomass ashes.

References

- [1] S. van Loo, J. Koppejan, *The Handbook of Biomass Combustion and Co-Firing*, Earthscan; United Kingdom, 2008.
- [2] ISO17892-1, *Geotechnical investigation and testing - Laboratory testing of soil - Part 1: Determination of water content*, 2014.
- [3] ISO17892-2, *Geotechnical investigation and testing - Laboratory testing of soil - Part 2: Determination of bulk density*, 2014.
- [4] ISO17892-3, *Geotechnical investigation and testing - Laboratory testing of soil - Part 3: Determination of particle density*, 2015.
- [5] P.P. Cunha, *Evolução Tectono-Sedimentar Terciária da Região de Sarzedas (Portugal)*, *Comunicações dos Serviços Geológicos de Portugal* (1987) 67–84.
- [6] S. V Vassilev, D. Baxter, L.K. Andersen, C.G. Vassileva, An overview of the composition and application of biomass ash. Part 1. Phase–mineral and chemical composition and classification, *Fuel*. 105 (2013) 40–76. <https://doi.org/10.1016/j.fuel.2012.09.041>.
- [7] S. V. Vassilev, D. Baxter, L.K. Andersen, C.G. Vassileva, An overview of the chemical composition of biomass, *Fuel*. 89 (2010) 913–933. <https://doi.org/10.1016/j.fuel.2009.10.022>.
- [8] D. Vamvuka, D. Zografos, Predicting the behaviour of ash from agricultural wastes during combustion, *Fuel*. 83 (2004) 2051–2057. <https://doi.org/10.1016/j.fuel.2004.04.012>.
- [9] D. Vamvuka, M. Pitharoulis, G. Alevizos, E. Repouskou, D. Pentari, Ash effects during combustion of lignite/biomass blends in fluidized bed, *Renew. Energy*. 34 (2009) 2662–2671. <https://doi.org/10.1016/j.renene.2009.05.005>.
- [10] D. Krutul, T. Zielenkiewicz, A. Radomski, J. Zawadzki, A. Antczak, M. Drozddek, T. Makowski, Metals accumulation in Scots Pine (*Pinus Sylvestris* L.) wood and bark affected with environmental pollution, *Wood Res*. 62 (2017) 353–364.
- [11] J. Fromm, Wood formation of trees in relation to potassium and calcium nutrition, *Tree Physiol*. 30 (2010) 1140–1147. <https://doi.org/10.1093/treephys/tpq024>.

- [12] S. V. Vassilev, C.G. Vassileva, A new approach for the classification of coal fly ashes based on their origin, composition, properties, and behaviour, *Fuel*. 86 (2007) 1490–1512. <https://doi.org/10.1016/j.fuel.2006.11.020>.
- [13] M. Sami, K. Annamalai, M. Wooldridge, Co-firing of coal and biomass fuel blends, *Progress in Energy Combustion Science*. 27 (2001) 171–214. [https://doi.org/10.1016/S0360-1285\(00\)00020-4](https://doi.org/10.1016/S0360-1285(00)00020-4).
- [14] S. V. Vassilev, D. Baxter, L.K. Andersen, C.G. Vassileva, An overview of the composition and application of biomass ash., *Fuel*. 105 (2013) 19–39. <https://doi.org/10.1016/j.fuel.2012.10.001>.
- [15] United States Environmental Agency Protection, Hazardous Wastes, 2020. <https://www.nj.gov/dep/srp/guidance/scc/#q>
- [16] A. Kabata-pendias, H. Pendias, *Trace Elements in Soils and Plants*, 3rd ed., CRC Press, 2001.
- [17] Official Journal of The European Communities, Directive 86/278/EEC, 1986.