Analysis of the chemical properties of almond and walnut shells for use in earthworks

T. Nouioua
GeoBioTec and FibEnTech, University of Beira Interior, Covilhã, Portugal

L. Marchiori
GeoBioTec and FibEnTech, University of Beira Interior, Covilhã, Portugal

F. Silva
GeoBioTec and FibEnTech, Polytechnic Institute of Bragança, Bragança, Portugal

A. Albuquerque
GeoBioTec and FibEnTech, University of Beira Interior, Covilhã, Portugal

L. Andrade Pais
GeoBioTec, University of Beira Interior, Covilhã, Portugal

V. Cavaleiro
GeoBioTec, University of Beira Interior, Covilhã, Portugal

ABSTRACT: Almond (AS) and walnut shells (WS) have attracted the interest of scientific community due to the possibility of developing innovative eco-friendly materials. This work aims to analyze the chemical characteristics of AS, WS, a residual granitic soil (RGS) and two mix-tures of waste:soil (10:90% and 40:60%) for evaluating their compatibility for earthworks application. Results show that both wastes could be incorporated into RGS for improving its properties and additionally can remove some water pollutants due to the presence of K2O, CaO and SiO2. This application could reduce the need to use soil natural resources, incineration of both wastes or their deposition in sanitary landfills and can promote their valorization and even create value-added products in the scope of the circular economy. However, additional studies are needed for a better understanding of their potential for using in earthworks, namely leaching, solubilization and adsorption experiments.

1 INTRODUCTION

The agroindustry sector produces significant quantities of agro-industrial wastes, and there is a growing interest among researchers in developing waste-based materials for construction of roads, paved areas and buildings (Khanjanzadeh *et al.*, 2014; Yao *et al.*, 2022), geotechnical applications as soil reinforcement and production of liner materials (Chen *et al.*, 2021) and environmental sanitation application as wastewater treatment technologies, irrigation canals and infiltration basins (Ayala & Fernandez, 2019; Dias *et al.*, 2021). These wastes can also provide other benefits such as low cost materials, availability, simplicity of operation and easy applicability for several purposes.

Almond and walnut processing industries generate high amounts of discarded wastes (Figure 1) worldwide, either in primary sectors (crop-based and fruit-base production) or by secondary processing industries (processing-based), the major part being lignocellulosic biomass. Almond shells (AS) and walnut shells (WS) are produced in primary and secondary sectors (Li *et al.*, 2018), and their physical and chemical characteristics have been studied by several researchers, but mainly for extraction of compounds for application in the pharmaceutical and petrochemical industries (Demirbaş, 2010; Queirós, 2020). Both residues include mainly lignin, cellulose, hemicellulose, ashes and tannins that can be extracted for creating other chemicals and materials (Demirbaş, 2010; Queirós, 2020), and have been mainly studied to be used as adsorbent material for heavy metal removal, namely for arsenic (As), cadmium (Cd), lead (Pb), mercury (Hg), nickel (Ni) and zinc (Zn) removal from mining muds (Ayala & Fernández, 2019; Mirmohammadmakki *et al.*, 2022), contaminated streams (Dias *et al.*, 2021), landfill leachate

(Ghaffariraad & Ghanbarzadeh, 2021), or for producing waste-based adsorbents (Wang *et al.*, 2021). Both wastes have also used to produce biochar for soil correction (Hamdouni *et al.*, 2022).

Figure 1. Shells generation from almond and walnut production.

Residual granitic soils (RGS) are product of granite rock's weathering, and its mineralogical composition is mainly quartz and orthoclase, with minor portion of plagioclase, mica, and kaolin. Geotechnical parameters of this soil can vary according to the weathering degree of the rock. Furthermore, for earthworks, the main problems around granitic soils are slope instability, variation in shearing strength and compressibility, high to medium hydraulic conductivity, and low cation exchange capacity, plasticity, and cohesion (Marchiori, 2022).

There are not many studies on AS or WS on their physical, geotechnical, and chemical characteristics associated to soil applications, especially as raw materials. Nnochiri & Emeka (2017) used 2%, 4%, 6%, 8% and 10% of burned WS for stabilized the properties of a lateritic soil and concluded that adding increasing doses of WS, the soil strength increased. Arama (2021) tested WS as an additive for foundations of highway embankments and observed that the increase of curing time and the quantity of wastes significantly affected the strength properties of kaolin. The inclusion of AS ashes along with lime for changing the properties of a kaolin soil was studied by Vydehi *et al.* (2021) and observed a reduction of soil's plasticity. The mixture of kaolin soil with 1% of WS and 0.5% of lime showed the maximum optimum moisture content and the lowest value of maximum dry density.

Therefore, AS and WS seems to present adsorption capacity for pollutants removal, especially for heavy metal removal and, therefore, their application in roads, wastewater treatment ponds, infiltration basins and ponds for mine tailings can bring an additional advantage in terms of reducing pollutants from wastewater. Therefore, these wastes could be used as a filler for tout-venant or for the construction of those earthworks, in mixture with soils, in proportions that do not reduce the soil properties required for those works and, additionally, can remove pollutants from wastewater, stormwater and road runoff. However, it is necessary to carry out adsorption, solubilization and leaching tests in samples of waste:soil mixtures.

The objective of this preliminary investigation is to analyze the chemical characteristics of AS, WS, a granitic soil and mixtures waste:soil to assess the advantages of both wastes to be incorporated into the soil and the potentially of classifying them as waste-based geotechnical materials.

2 MATERIALS AND METHODS

AS and WS were collected at local industries located in Macedo de Cavaleiro (Portugal). The shells were separated, triturated and sieved in a four-step sequence as shown in Figure 2: first, the seeds were removed remaining only the shells, then the shells were smacked with a hammer and triturated with a kitchen cutting machine, then sieved in 2.0 mm. Portions above and below 2.0 mm were selected. That grain size was selected for replacing fine material in sandy soils. The RGS was collected from Penalobo, Guarda (Portugal) (Figure 3). Two mixtures of waste:soil were prepared for each waste (As and WS), using dried masses as follows (Figure 3): AS10:90% (10% of AS and 90% of RGS); AS40:60% (40% of AS and 60% of RGS); WS10:90% (10% of WS and 90% of RGS); WS40:60% (40% of WS and 60% of RGS). For each sample, chemical analysis was determined through X-ray fluorescence (XRF), using an energy dispersive spectrometer S-2700 Hitachi equipment.

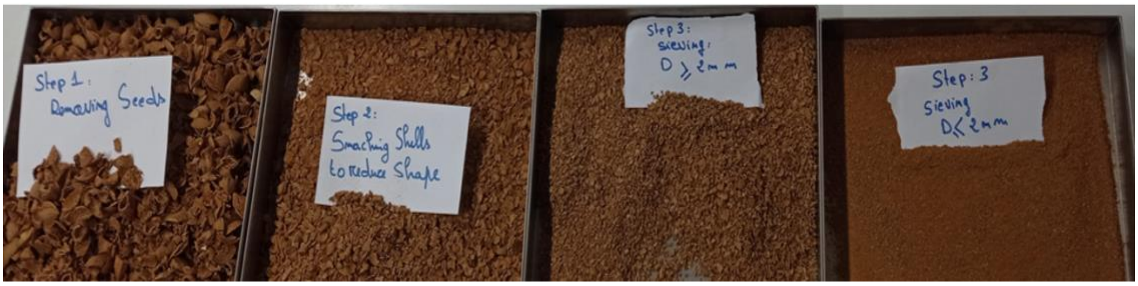

Figure 2. Sampling procedure for preparing AS and WS.

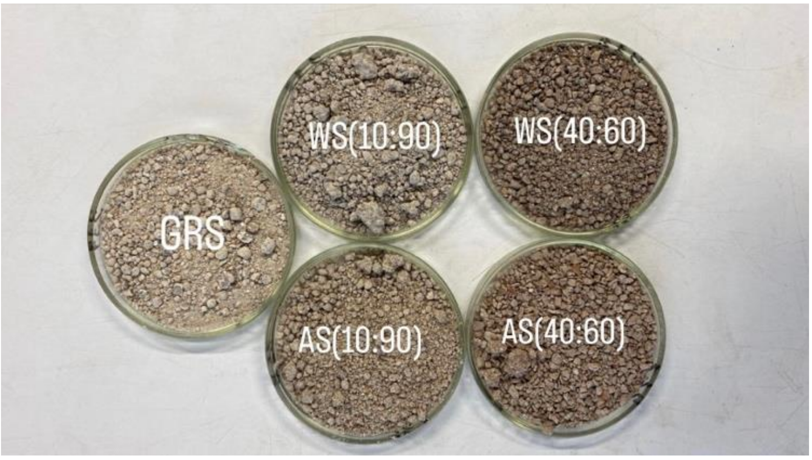

Figure 3. Samples for testing: a) soil; b) AS 10:90%; c) AS 40:60%; d) WS 10:90%; e) WS 40:60%.

3 RESULTS AND DISCUSSION

Oxides percentages of AS and WS are presented in Table 1, and results obtained from Queiros et al. (2020), Valverde et al. (2013) and Dias et al. (2021) were included for comparison. Approximately 74.2% of the chemical constitution of AS is concentrated in three parameters (K_2O (42.2%), CaO (26.3%) and SiO_2 (5.7%)), while for WS around 94.1% is concentrated in five parameters (K_2O (27%), CaO (53.9%), P_2O_5 (4.1%), Fe_2O_3 (5.9%) and SiO_2 (3.2%)), with K more abundant in AS and Ca more abundant in WS. Li et al. (2018) also mention that K, Ca and Si are the main compounds of AS. XRD analysis carried out by Soriano et al. (2021) found crystalline phases in AS partially calcinated with calcite ($CaCO_3$), fairchildite ($K_2Ca(CO_3)_2$) and bütschilite ($K_2Ca(CO_3)_2$), which justify the higher values for Ca and K, and also presents an amorphous fraction with quartz (SiO_2), which justifies the presence of Si. Crystallization in raw AS and WS is mainly caused by cellulose and is presented in approximately 32.9% and 23.7%, respectively (Li et al., 2018), and may result in a decrease of mechanical properties, but both wastes present high degree of amorphosity (Uddin & Nasar, 2020).

The results are like those found by Queiros et al. (2020), although this author found higher values for K, Mg, P, S and Fe in the AS, and for Mg, P, S and Fe in the WS and did not find Si in any of the wastes. Valverde et al. (2013) observed percentage values closer to those of this study for the AS, but with less content of K and Ca. Dias el al. (2021) found higher percentages of K, Mg and P, and lower percentages of Ca and Si, than those observed in this study for WS. Si is an element present in both wastes and Geyikçi (2016) has successfully extracted it from AS using alkali leaching and subsequent burning. The high value for K indicates that both wastes have potential behavior as alkaline activators as also found by Soriano et al. (2021).

Oxides percentages for the four mixtures and the soil are presented in Table 2. When introducing both wastes in the RGS, Si and Al contents increase significantly, compared with the raw wastes (Table 1), due to the presence of quartz (Si) and orthoclase and kaolin (Al and K) in RGS (Marchiori, 2022), whilst Ca, K and P decreases. Ca, K, P and Fe decreases. This decrease can be advantageous since high content of Ca, K and Fe can impact in plants physiology, since they can be toxic for plants in high concentrations, and low values have low impact. Soil pH can increase and can lead to increase in the cation exchange capacity (CEC), which can be advantageous for the removal of pollutants present in some wastewater.

Oxides percentages were normalized discarding loss on ignition (LOI) values, looking for the possibility of thermal treatment of shells. The values of LOI are 4.5%, 45% and 30%, or RGS, AS and WS, respectively, and thermal treatment may be carried out to improve crystalline phase (Geyikçi, 2016) and enhance pozzolanic properties, but burning wastes is nowadays an unsustainable practice due to the release of CO_2. Several heavy metals are presents in both wastes (Cr, Cu, Fe and Zn) but in small quantities. However, leaching and solubilization experiments must be carried out to evaluate the potential migration of those pollutants to groundwater.

Table 1. Elementary composition in oxides (%) for AS and WS.

Parameter [%]	AS			WS		
	Queirós *et al.* (2020)	Valverde *et al.* (2013)	Authors	Queirós *et al.* (2020)	Dias *et al.* (2021)	Authors
Na_2O	1.44	0.95	0.00	2.40	0.51	0.00
K_2O	52.6	17.6	42.2	20.1	40.0	26.9
CaO	14.2	2.22	26.2	40.8	46.4	53.8
MgO	5.40	1.51	0.23	8.24	3.30	0.25
P_2O_5	5.70	1.21	4.08	6.81	5.22	4.10
SO_3	4.68	0.65	1.03	6.35	1.09	1.08
Fe_2O_3	15.2	0.27	9.74	14.2	0.71	5.91
Cu_2O	0.02	0.02	3.54	0.02	0.00	0.53
ZnO	0.08	0.02	3.20	0.07	0.00	0.21
MnO	0.25	0.02	0.38	0.46	0.41	0.70
Al_2O_3	0.00	0.00	1.95	0.00	1.41	1.07
SiO_2	0.00	0.00	5.71	0.00	0.82	3.17
ClO	0.00	0.00	0.17	0.00	0.00	0.87
TiO_2	0.00	0.00	0.42	0.00	0.00	0.52
CrO	0.00	0.00	0.17	0.00	0.00	0.00
PbO	0.00	0.00	0.18	0.00	0.00	0.00

Physically analyzing, the inclusion of both waste materials can lead to decrease in density and increase of water absorption when mixed into granular soils, because they are more porous and lighter than soils, as observed by Marchiori et al. (2022a), for water treatment sludges, and by Marchiori et al. (2022b) for biomass ashes. Changes in chemically composition of the mixtures waste:soil may impact in cation exchange capacity, pozzolanic activity, and stabilization of clayey soils. Earthworks use many methodologies and technologies to enhance soils properties, from construction of retaining structures to filter layers. The use of these wastes as an alternative source of geomaterials for earthworks can be a cheaper alternative because wastes are low-cost materials and opens the possibility of producing new materials with added value. Results show that these wastes could be tested for enhancing soils properties, replacing fine material (fillers) and removing some pollutants from water in earthworks. A lack of studies is observed on the physical and mechanical properties of AS and WS such as granulometric curve, density, specific gravity, specific surface, cation exchange, permeability, cohesion, friction angle, and shear strength among others, for a better understanding of the potential of these wastes to be used in earthworks.

Table 2. Elementary composition in oxides (%) for AS and WS mixtures with soil.

Parameter [%]	RGS	AS10:90%	AS40:60%	WS10:90%	WS40:60%
Na_2O	1.96	1.84	1.81	1.84	1.85
K_2O	4.08	3.83	3.98	4.10	4.05
CaO	0.63	0.65	0.82	0.65	0.77
MgO	1.07	1.12	0.91	1.10	0.99
P_2O_5	0.40	0.40	0.45	0.36	0.37
SO_3	0.02	0.02	0.09	0.01	0.04
Fe_2O_3	1.88	1.83	1.91	1.94	2.01
Cu_2O	0.00	0.02	0.06	0.01	0.01
ZnO	0.01	0.01	0.02	0.01	0.01
MnO	0.08	0.07	0.08	0.07	0.08
Al_2O_3	27.87	27.16	23.12	27.85	25.60
SiO_2	56.85	55.40	46.81	56.16	51.48
TiO_2	0.11	0.11	0.10	0.11	0.12
CrO	0.01	0.02	0.01	0.01	0.01
PbO	0.00	0.02	0.02	0.01	0.01
F_2O	0.00	0.32	0.39	0.38	0.42

4 CONCLUSIONS

This study gives positive indications on the use of AS and WS for enhancing RGS properties for earthworks applications. AS and WS are mainly composed by Ca, K, Fe, P and Si and, after incorporated in soil, the main compounds become Si, Al, and K, due to the abundance of quartz, orthoclase, and kaolin in RGS. High K values indicates that both wastes have potential for alkaline activation. Small quantities of Ca, K and Fe can upper soil pH and CEC, which may allow an additional capacity for removing heavy metals and other water pollutants present or circulating through earthworks. The addition of both wastes can lead to decrease in density and increase of water absorption as they are more porous and lighter than soils. However, additional physical, chemical, and mechanical characterization, besides leaching, solubilization and adsorption experiments, are needed to allow a better understanding of their potential to be incorporated in earthworks.

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