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Recycling of washed olive pomace ash for fired clay brick manufacturing

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HIGHLIGHTS

- Pretreated ash from olive pomace is used as raw material for brick manufacturing.
- Pretreating ash by leaching is also useful for obtaining potassium-rich solutions.
- Leached ashes are a pore former in bricks improving thermal conductivity.
- Mechanical properties of resulting bricks fulfill product requirements.

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ABSTRACT

Milled or micronized washed olive pomace ash was used to replace different amounts (5 and 10 wt%) of clay in brick manufacture. The properties of these bricks were compared to conventional products following standard procedures. Bricks formed with ash showed a decrease of 0.13–0.16 W/m K in thermal conductivity. With a minimum bulk density and bending strength of 1790–1810 kg m^{-3}, and 10–12 N mm^{-2}, respectively, fired bricks fulfil standard requirements for clay masonry units. Milled ash performs better than micronized ash. The ash leachate is a valuable source of potassium for the manufacture of fertilizers.

1. Introduction

Biomass ash is the solid residue from biomass incineration. Nowadays, an increasing number of biomass-based power plants for heat and electricity production are in operation so the amount of available ash is also growing. Fields of application for biomass ash depend on biomass ash features such as morphology, chemical and mineralogical composition and leaching behaviour. The main classification criteria of ashes differentiate between: (1) fly ash and bottom ash (type of ash), and; (2) among ash from fluidized bed gasification, fluidized bed combustion, grate stokers and entrained flow gasification (type of incinerator–gasifier). Ash environmental management can be ordered from the least to the most attractive alternatives as follows: landfill, disposal other than landfill, disposal with energy conversion, recovery, material recycling, product reuse and prevention of ash production [1]. The selected alternative must be a bulk utilisation option. The main alternatives are utilisation as fertilizer (raw material), applications in geotechnical constructions and in industrial processes, and reuse as fuel [2].

Olive oil production is one of the most important agro-industries in Mediterranean countries, with Spain being the world leader in the production of olive oil. During the period 2000–2010 Spain produced an average of 5.4 millions of tonnes (Mt) per year of olive fruits from which 1.1 Mt/year of olive oil was extracted [3]. Most of the industrial facilities for olive oil production in Spain operate under the so-called two-phase centrifugation system and generate huge amounts of olive pomace, the residue obtained after separating the olive oil. Olive pomace, also referred to as olive wet cake, olive wet husk, *alperujo*, or two-phase olive mill waste, consists of components present in the fruits other than oil, e.g. pieces of crushed olive stones (15% w/w), olive pulp with residual oil (20% w/w), and water (65% w/w), a fraction of which is added during the olive oil extraction process [4].

As the average oil content of olive fruits is about 20% by weight, 80% of the fruit together with the added process water forms olive pomace, which still includes a small, variable proportion of residual oil. This residual oil is usually recovered by solvent extraction after drying the olive pomace, and the process generates another waste called dry olive cake or *orujillo* that can be used as

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fuel. In Andalusia, the main Spanish olive oil producing region, the olive pomace used for olive cake oil production accounts for approximately 70%, the other 30% being partly dried (40% moisture content) to facilitate the combustion in power plants [5].

In Andalusia, 18 biomass electric plants and biomass cogeneration plants operated in 2011 with an installed power capacity of 208.7 MW, and newer plants were planned. Both olive pomace and dry olive cake are rich in organic matter and potassium, and their lower heating values (14–20 MJ/kg) yield valuable waste as fuels for thermal and/or electrical production [6]. However, a drawback of the use of the above waste as fuels is the great amount of biomass ash generated as end waste (between 4 and 8% of the burned waste). The common disposal of biomass ash is landfill in sites next to the power plants, but this alternative is the least attractive in the ash environmental management. Various studies focused on ash produced by olive waste combustion as raw materials for cement-based products [7] and building materials [8], their potential use as soil amendment [9] and their characterisation as fertilizers [10]. Other studies described potential uses of biomass gasification [11,12] or combustion ash [13] as a raw material for extruded brick manufacturing, but little information is available on the application of ash from combustion of olive oil residues. On the other hand, several authors suggest the use of other olive mill effluents such as olive mill wastewater [14,15], and olive pomace [16] as a raw material for ceramic materials.

The aim of this work is to assess for the first time the use of olive pomace ash as a raw material in fired clay formulations by extrusion moulding processes, and to check the physical and mechanical properties of the new materials. This work is part of a broader study about the valorisation of the different olive mill wastes [17,18]. A prerequisite for the above assessment is to investigate the pretreatment required for the ceramic use of olive pomace ash.

2. Materials and methods

2.1. Clay

The clay used was provided by Cerámica Malpesa, S.A. (Bailén, Spain), a local ceramic industry. It represents a common type of illitic brick clay across the Mediterranean countries, with intermediate carbonate content and firing temperature. The chemical composition and the mineralogical characterisation of the clay were described in a previous study [17]. In summary, the clay contains 59% phyllosilicates, 30% quartz, 9% calcite and trace amounts of dolomite and feldspars. Phyllosilicates include 60% illite, 35% kaolinite and 5% pyrophyllite. The clay chemical composition is presented in Table 1 and allows the clay to be classified as red firing clay.

2.2. Characterisation of olive pomace ash (A) and washed olive pomace ash (WA)

Olive pomace ash (A) was collected from the bottom of the incinerator of a local industrial facility of olive cake extraction where olive pomace is used as a fuel. The composition of the olive pomace ash depends on the olive pomace composition and the incinerator operation conditions [10]. The mineralogical characterisation of the ash was determined using X-ray diffraction using a Siemens D5000 diffractometer with Ni-filtered Cu Kα radiation, with a voltage of 35 kV and current of 35 mA. The main oxides present in the olive pomace ash were determined by X-ray fluorescence, using a Pioneer S4 Explorer device by Bruker. The carbonate content (expressed as calcium carbonate) was determined by calcimetry in a Bernard calcimeter. The main features of olive pomace ash, alkalinity and the soluble salt content, detrimentally affect the ceramic production process and manufactured product. Furthermore, these features represent an environmental risk for soil and water in ash management [19]. Thus, prior to mixing with the clay, olive pomace ash was properly pre-treated. The potential influence of ash grain size in the physical and mechanical properties of ceramic body was the reason for milling and micronizing washed olive pomace ash [20].

In the present work, olive pomace ash was used at laboratory scale in two ways after a pre-treatment process. The pre-treatment process consisted of a group of either three or four operations: milling, washing and drying; or milling, washing, drying and micronizing. At the industrial scale, laboratory test results and other factors would determine whether drying and micronizing are required.

First, olive pomace ash was milled in a hammer mill incorporating a 1 mm round-hole sieve. Second, milled olive pomace ash and water were stirred in a beaker for 1 h at 45 °C. The ash/water ratio was 1:4 (w/w). Third, the ash suspension was filtered through a 2.7 μm particle-retention hardened filter, and the leachate through a 0.22 μm nitrocellulose filter for chemical analysis. Finally, the filter cake, i.e. WA was dried in an oven at 110 °C until dry. For the clay body with micronized and washed olive pomace ash (MWA), a final operation was carried out in a vibratory disc mill. The micronization consisted of 50 g batch grinding for 4 min at 1400 rpm in a 250 ml tungsten carbide grinding set.

Grain size distributions of olive pomace ash, both milled and micronized, were measured in a Retsch sieve shaker for 15 min in 2 mm amplitude discontinuous vibration mode.

The grain size distribution of the WA is presented in Table 2. Milled and micronized ashes differ significantly in grain size distribution. In micronized ash, the fraction <0.063 mm represents 98% whereas in milled ash it only reaches 23%.

2.3. Characterisation of leachates from olive pomace ash

The conditions for olive pomace ash washing were previously established. At a ratio 1:4 (w/w) by stirring in a beaker for 1 h at 45 °C, a milled olive pomace/water suspension was leached in two tests: (1) a single stage leaching; (2) two-stage cross-current leaching. In both tests, after the stirring time, the ash suspension was filtered through a 2.7 μm particle-retention hardened filter. In the cross-current test, the quantity of fresh water used in the second stage was the same as that in the first stage in spite of the cake weight from the first cross-current leaching stage is lower than the weight of ash entering the first stage. Leachates from single stage leaching and from the second stage in the two-stage cross-current leaching were filtered through a 0.22 μm nitrocellulose filter for chemical analysis. In the single stage leaching, the water ratio retained in the leached ash was 0.28 (w/w) and the ratio of extract to water was 0.94 (w/w).

Leachate characterisation was conducted as follows:

- pH and electrical conductivity by potentiometry, according to adapted methods of the standards UNE-EN 10523:2012 and UNE-EN 27888:1994, respectively, by using a Metrohm Robotic USB 855 XL instrument.
- Dry matter by gravimetry.
- Alkalinity by a titrimetric method, following an adapted method of UNE-EN ISO 9963-1:1996 by using a Metrohm Robotic USB 855 XL instrument.
- Manganese and iron by ICP-MS, according to adapted methods of the standards ISO 17294-1:2004 and ISO 17294-2:2004 with an Agilent 7500 CE instrument.
- Other cations and the anions by ionic chromatography according to adapted methods of the standards UNE-EN ISO 14911:2000 and UNE-EN ISO 10304-2:2005, respectively. For cations and anions, the instruments used were Metrohm 881 28810030 and Compact IC PRO 28810010, respectively.

2.4. Extrusion trials, drying and firing of bodies

The extrusion trials were performed with one of the ceramic bodies currently being used in Cerámica Malpesa, S.A. for red facing bricks (RB). The mixture of clay was taken from the milling device of the industrial plant and was passed through shaking screens provided with 1.0 × 1.2 mm rectangular holes. The moisture content of the milled clay was typically 6–10%.

The ceramic body for extrusion was prepared by mixing the clay mixture with washed olive pomace ash (WA) or micronized washed olive pomace ash (MWA) and fresh water (FW) in a lab mixer. Two clay bodies with 5% and 10% WA (namely,

Table 1
Chemical composition (main oxide content, %) of RB clay and olive pomace ash, as collected (A), and washed (WA).

	Main oxide content (%)										
	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	LOI
RB clay	53.27	15.97	6.39	0.06	1.92	5.88	0.4	3.82	0.77	0.14	9.69
Olive pomace ash											
A	16.44	7.03	2.16	0.04	6.83	35.43	<LOD	19.69	0.20	6.01	5.60
WA	18.54	7.66	2.37	0.05	7.14	37.78	<LOD	11.31	0.25	6.51	8.57

LOI: loss on ignition, LOD: limit of detection.