Construction and Building Materials 68 (2014) 659–666

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Replacement of the mixing fresh water by wastewater olive oil extraction in the extrusion of ceramic bricks

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HIGHLIGHTS

- OW or OOW could replace mixing FW in the process for extrusion clay bricks.
- OW or OOW produced improvements in the mechanical and thermal properties of bricks.
- The incorporation of wastes modified the porosity of the mixture bricks.
- Bricks met the UNE standards and can thus be used as green construction materials.

ARTICLE INFO

Article history:
Received 25 March 2014
Received in revised form 10 June 2014
Accepted 3 July 2014

Keywords:
Wastewater olive oil
Clay brick
Recycling
Sustainability
Physical, mechanical and thermal bricks properties

ABSTRACT

This investigation deals with the possibility of incorporating effluents resulting from olive oil extraction activity, as wastewater from olive-washing stage (OW) or wastewater from olive-oil washing stage (OOW), in the brick-making process. The feasibility of replacing mixing fresh water (FW) by OW or OOW of the extraction process of olive oil, in the process for manufacturing clay bricks, has been studied. FW, OW or OWW (22 wt%) was added to the clay in order for it to acquire enough plasticity to the stage of molding by extrusion. Samples containing OW or OOW were found to be comparable in extrusion performance to a control product that used FW. Once extruded, test specimens were dried at 110 °C (24 h) and fired at 850 or 950 °C (3 °C/min) for 4 h. The influence of replacing fresh water by wastes on the technological behavior of fired bricks was assessed by linear shrinkage, bulk density, water suction, water absorption and apparent porosity. Their mechanical and microstructural properties were also investigated by compressive strength and scanning electron microscopy (SEM), and thermal behavior by thermal conductivity. Results indicated that replacement of FW by OW or OOW produced slight improvements in the physical, mechanical and thermal properties of bricks. This may have been due to porosity generated by these wastes mainly closed pore type.

Therefore, the use of these residues can alleviate the environmental impact generated by the industry of extraction of olive oil and, at the same time, represent an economic and water saving for the ceramic industry.

1. Introduction

The olive oil industry is very important in Mediterranean countries. Spain is the main world producer. More than 80% of the national production is concentrated in Andalusia, a region in the South of Spain, specially in the provinces of Jaén and Córdoba. There are two centrifugation methods called three-phase and two-phase for olive oil extraction. The three-phase method generates three fractions at the end of the process: one solid (wet pomace) and two liquid (oil and wastewater). In Spain the two-phase method replaced the three-phase one due to a reduction in water consumption and production of two fractions: a solid one (wet pomace or "alperujo"), and a liquid one (olive oil). However, olive oil production still generates some wastewater coming out basically from olive washing, before entering the extraction process and the olive oil after the centrifugation stage. Wastewater is a dark-colored liquid containing many dissolved and suspended substances, therefore presenting high-polluting charge. The dry effluent has a heavy load of organic matter, mainly consists of polyphenols, polysaccharides, sugars, polyalcohols, proteins, organic acids and oils [1]. Moreover, contain considerable amounts

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http://dx.doi.org/10.1016/j.conbuildmat.2014.07.017
0950-0618/

of suspended solids [2]. Wastewater is typically sent to evaporation in storage ponds due to its low investment and, however, it needs large areas and produces several problems such as bad odor, infiltration and insect proliferation [3].

Since around 80% of processed olives happen to be a residue [4,5], they generate between 3 and 4 million tons of waste a year. These high levels of waste generation have caused in recent years many research works allowing disposal or reuse. Several authors have studied the valorisation of solid waste fraction, *alperujo* [3,6–11]; and olive mill wastewater from three-phase extraction system [12–15].

In addition, it has been estimated that every ton of processed olives in the two-phase extraction process produced 100–120 m^3 of olive washing (OW) and 200 m^3 of olive oil washing (OOW), obtaining 200 kg of olive oil [3]. As the production of olive oil reached 618,200 tons during the 2012/13 campaign in Spain [16], the production of wastewaster is significant to consider its valorisation. De la Casa et al. [17] studied the valorisation of wastewater from two-phase olive oil extraction in fired clay brick production concluding that the technological properties are not affected by the use of the residue.

The ceramic industry processes have made waste recovery specially viable by incorporating residue into the internal structure of the matrix clay [18] as raw material in the brick production. Rapid ways for implementing principles of sustainable development have been emerging within the construction, as well as a trend to achieve building with minimal energy consumption. The employment of ceramic products manufactured from waste in building is an option that fits perfectly with the principles of sustainable development, since it implies a value solution that allows the reuse of materials that today are considered to be waste and, on the other hand, can give to the ceramic material better performance.

In this study, water used for olive washing or olive oil washing in the two-phase olive oil extraction system have been used as a substitute for fresh water in brick manufacturing. The main aim of this work is to study the effect on the technological properties of ceramic bricks by using wastewater in comparison to bricks obtained using fresh water.

2. Experimental

2.1. Preparation of the samples

Clay was supplied by a clay quarry located in Bailen, Jaén (Spain) and was obtained by mixing three types of raw clay in equal parts: red, yellow and black clay (Table 1). The incorporation of red clays allowed modified the technological behavior of yellow and black clays. Red clay, low carbonated and with higher alumina content, does not have sufficient plasticity for the shaping of resistant unfired pieces. Due to the proportions of clays used, the mixture of clays has appropriate plasticity (plasticity index:9.6%) for shaping and presents medium carbonate content (13.52%).

Clay was crushed and ground to yield a powder with a particle size suitable to pass through a 150 μm sieve. The waste, olive wastewater and olive oil wastewater were supplied by a local olive oil extraction plant and used directly without any prior pretreatment. The ceramic paste for the extrusion was prepared by adding fresh water (FW) or residue resulting from olive oil extraction (OW or OOW) to the clay in a mixer. The amount of added water in the mixer depends on clay plasticity and on its consistency while performing the extrusion. In the present work 22 wt% of FW, OW or OOW was added as the clay. The same value as used at industrial scale for this kind of clay mixture. Extrusion was carried out in a laboratory Venco extruder. Solid bricks with 30 × 10 mm cross sections and a length of 60 mm were obtained. Extruded test pieces were dried at room temperature for about 24 h, and then heated in an oven at 110 °C until constant weight for at least 24 h. Samples were fired in a laboratory furnace at a rate of 3 °C/min up to 850 or 950 °C for 4 h. Samples were then cooled to room temperature by natural convection inside the furnace. The shaped samples were designated as C-FW-x for the bricks with fresh water, C-OW-x for the mixture with olive wastewater and C-OOW-x for the mixture with olive oil wastewater, being *x* the firing temperature.

Table 1
Chemical composition of the fired clay.

Oxide content (%)	Red clay	Yellow clay	Black clay	Mixture of clays
SiO_2	53.94	53.54	45.50	47.17
Al_2O_3	15.93	11.78	11.55	12.51
Fe_2O_3	14.22	7.02	5.82	6.49
CaO	3.84	13.67	21.45	13.52
MgO	1.81	2.20	2.10	2.11
MnO	0.032	0.063	0.10	0.05
Na_2O	0.22	1.72	1.40	0.31
K_2O	7.95	4.17	3.43	3.61
TiO_2	1.54	1.56	1.21	0.78
P_2O_5	0.21	0.10	0.10	0.14
SO_3	–	–	2.91	1.58
NiO	–	–	–	0.0086
CuO	–	–	–	0.0017
ZnO	–	–	–	0.0082
Ga_2O_3	–	–	–	0.0027
Rb_2O	–	–	–	0.017
SrO	0.035	0.096	0.22	0.043
ZrO_2	–	0.059	0.141	0.035
Nb_2O_5	–	–	–	0.0021
BaO	–	–	–	0.047
LOI	–	–	–	10.6

2.2. Characterization of brick raw materials

The acidity of the OW and OWW was determined with Crison pH meter Basic 20. The electrical conductivity was electrometrically measured using a Crison Basic 30 EC conductivity meter. The determination of the organic content of dry residue was performed according to ASTM D-2974, Standard Test Method for Moisture, Ash, Organic Matter of Peat and Other Organic Soils [19]. The ignition temperature was 440 °C. The total content of carbon, hydrogen, nitrogen, and sulfur of dry residue was determined by combustion of samples in O_2 atmosphere using the CHNS-O Thermo Finnigan Elementary Analyzer Flash EA 1112. The higher heating value (HHV) was determined using a Parr 1341 Plain Oxygen Bomb Calorimeter.

Chemical oxygen demand (COD) were established through potassium dichromate digestion and, the amount of oxygen required to biodegrade the organic material present in the waste is evaluated by the biochemical oxygen demand (BOD_5) using a BOD sensor Velp Scientific.

The plasticity of the samples was measured from the Atterberg Limits (Plastic Limit, LP, and Liquid Limit, LL) and Plasticity Index (IP).

In the present work, FW, OW or OOW was added to 22 wt%, the results indicated that the plastic limit or amount of minimal water to mold the mixture decreased when using OW (19.7%) or OWW (20.1%) as mixing water. These results demonstrated that the volume of OW or OWW amount needed to produce the optimum extrusion performance is smaller than that the fresh water was used (21.9%). This would be attributed to an additional lubricating effect performed by the addition of the wastes. Similar results were previously found in the extrusion effect when adding olive oil mill wastewater (OMW) [13,14]. However, the plasticity index that establishes a range of moisture content in which the clay is moldable, decreased when FW is replaced by OW or OOW from 9.6% to 6.1% and 5.9% respectively.

The Qualitative determination of major crystalline phases was achieved using the Philips X'Pert Pro automated diffractometer equipped with a Ge (111) primary monochromator. Chemical composition was determined by X-ray fluorescence (XRF) using the Philips Magix Pro (PW-2440). Thermal behavior was determined by thermogravimetric and differential thermal analysis (TGA-DTA) with a Mettler Toledo 851e device in oxygen operating at a ramp of 20 °C/min from room temperature to 1000 °C.

2.3. Characterization of the bricks

Linear shrinkage was obtained by measuring the length of the samples before and after the firing stage, using a caliper with a precision of ±0.01 mm, according to ASTM standard C326 [20]. Water absorption values were determined from weight differences between the as-fired and water-saturated samples (immersed in boiling water for 2 h), according to ASTM standard C373 [21] Open porosity (in vol.%) were determined from weight difference between saturated mass and dry mass with respect to exterior volume and closed porosity (in vol.%) was calculated from weight difference between dry mass and suspended mass in water with respect to exterior volume according to ASTM standard C373 [21]. Bulk density was determined by the Archimedes method [21]. The test to determine water suction was implemented according to standard procedure UNE 67-031 [22].

Tests of compressive strength were performed according to standard UNE-EN 772-1 [23] on a Suzpecar CME 200 SDC laboratory press. For this trial, six fired samples were studied. The area of both bearing surfaces was measured and the average