**“Re-Using an Oleic By-Product in the Manufacturing of Fired Clay Bricks”.**

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**Abstract.** The objective of this article is to contribute to the profitability of the olive growing by an optimal valorisation of its liquid residue (the margins) in building materials and more precisely in the fired clay bricks by substituting the water used in this manufacture by the liquid margins with percentages from 10 to 30%, and to study the effect of this substitution on the characteristics of the produced bricks. The experimental study consists of the elaboration of clay and margins-based sample bricks at laboratory scale. The optimum substitution rate of the margins used in the bricks formulation was assessed by mechanical tests. Parameters such as porosity, water absorption, and bulk density influencing the behaviour of the bricks were determined.

**Keywords:** Oleic By-Product; margins; fired bricks; Clay; Manufacturing.

**I Introduction**

Olive growing, with all its related activities, especially the extraction of olive oil, is an integral part of Morocco's heritage. However the by-products generated by this ancestral activity have a harmful impact on the environment, particularly on water resources.

The liquid fraction (margins) is generated in a big quantity during the olive oil extraction and is considered the most polluting product for the environment [1]. Indeed, several studies have confirmed the harmful effects of margins on the microbial flora of the soil [2], on aquatic ecosystems [3], and even on the air [4]. Their quantity and composition vary according to the extraction process used [5], the variety of the olive tree and the degree of maturity of the olive [6]. Their treatment has become a national concern because of their high organic load and their resistance to biodegradation due to the presence of polyphenols.

On the other hand, several studies have shown the absorption capacity of phenolic compositions by clays [7], hence the idea of using these margins in their raw state in the manufacture of bricks construction delete, by substituting the used water by liquid margins with percentages ranging from 10 to 30%, and studying the effect of this substitution on the characteristics of the bricks produced [8].

**II-Materials and methods**

The margins used in this study were brought from three crushing units equipped with a three-phase continuous system located in three different cities: Ouazzane margins (MO), Fez margins (MF) and Ksar el Kebir margins (MK). These margins, used in this study, were collected during the olive growing season (November 2020 - February 2021). The samples were taken from the margins' storage tank, homogenised and kept at 6°C to minimise any change in characteristics. The natural clay was supplied by a brick factory located in Tangier city. To determine the properties of the margins, clay and bricks resulting from the mixture, chemical, physical and geotechnical studies were carried out.

**1-Physico-chemical Characterisation of Margins**

The physico-chemical characterisation of the margins was based mainly on the study of the following parameters: acidity (pH), electrical conductivity (EC), dry matter (DM), suspended solids (SS), chemical oxygen demand (COD), and total polyphenols. All samples were homogenised before analysis. Each result represents an average of three analytical tests performed.

**2- Characterisation of Natural Clay**

The physical and geotechnical properties of natural clay used in this study were investigated. Therefore, the following tests were carried out. Particle size analysis; Atterberg limits; Sand equivalent to 10% of fines; Bulk and Apparent density (porosity).

**3-** **Preparation of Laboratory-scale Bricks**

The preparation of the brick specimens in a cylindrical form (30 mm in diameter and 30 mm length) figure (1) was carried out using an extruder figure (2) in order to remove the air from the mixture to avoid cracking of the bricks during the firing process at 980°C.

The brick samples are performed by substituting the water used in the standard mixture (water-clay) with margins by varying the substitution rate of 10%, 20% and 30%.



**Fig.1**: Photo of brick samples after extrusion **Fig.2**: Photo of the extruder

**III. Results and discussions**

**1- Physico-chemical Results**

The results of physico-chemical analysis carried out on the margins are showed in table 1.

**Table 1**: Physico-chemical analysis of the studied margins

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  | pH | EC (mS/cm) | DM  (g/l) | SS (g/l) | COD  (mg ’O2/l) | Cl-  (g/l) | P.P  (g/L) |
| (MO) | 4.58 | 22.72 | 23.6 | 72.20 | 21600 | 14.2 | 8.34 |
| (MF) | 4.85 | 14.56 | 31.4 | 84.33 | 100800 | 7.81 | 5.16 |
| (MK) | 5.31 | 12.74 | 29.5 | 81.00 | 91200 | 6.39 | 5.11 |

**pH**

pH

**Fig. 3**: pH of the different margins

The pH measurement gives values between 4.58 and 5.31. The margins are therefore acidic effluents, due to the presence of organic acids. The value recorded in our study corresponds to the one quoted in the literature (4.5 to 6) [9].

The acidity of the margins increases with the duration of their storage. This phenomenon can be explained by auto-oxidation and polymerisation reactions that transform phenolic alcohols into phenolic acids. These reactions are manifested by a change in the initial colour of the margins from brown to a very dark black [10].

**EC (mS/cm)**

**Electrical conductivity EC mS/cm**

**Fig. 4:** Electrical conductivity of the different margins

The conductivity values vary between 12.74 mS/cm for (MK), 14.56 mS/cm for (MF) and 22.72mS/cm for (MO). These results are consistent with the results found in the literature [11]. These values give an idea of the high salt content present in these margins samples, which is due to the practice of salting for the preservation of the olives before crushing, and also to the natural richness of the margins by the dissolved mineral salts [12].

**Solide suspended g/l**

**Fig. 5:** Quantity ofSuspended solids in the different margins

The margins are very rich in suspended solids between (23.6 and 31.4) this value is similar to those reported by several studies. Some research results give low TSS values [13], [14], [12]. These results are explained by the origin of the sampling of the margins, in fact, these are taken from storage tanks in an average duration of 14 days and the TSS decreases under the effect of decantation.

**DM g/l**

**The dry matter DM g/l**

**Fig .6:** Concentration of the dry matter in the different margins

**COD mg O2/L**

**Chemical oxygen demand mg O2/L**

**Fig. 7**: Chemical oxygen demand of the different margins

The margins are very rich in organic matter expressed in terms of COD (chemical oxygen demand). The values obtained for the three sites are 21.9 g/l for (MO); 100.8g/l for (MF) and 91.2 g/l for (MK). These values obtained are almost comparable to those obtained by [15] which are in the order of 78 g/l and are also consistent with the results obtained in another research [16], [17] which are also between (50-150g/l). The COD values remain slightly lower than the results quoted in literature [18], [19], [20], this is due to the degradation of the margins in the course of time in the storage ponds, and with time, the organic matter degrades.

**Cl- g /L**

**Chlorides g/L**

**Fig. 8:** Concentration of the chloride in the different margins

The chloride ion contents vary respectively between 14.2(MO), 7.81(MF) and 6.39(MK). These results are similar to those obtained by [18]; this high chloride content is due to the practice of salting (addition of salt in large quantities) to preserve the olives before the extraction process.

**Polyphenol concentration g/l**

**TPP g/L**

**Fig. 9**: Polyphenol concentration in the margins

The content of phenolic compounds is between 5.11g/ and 8.34 g/l, these results are compatible with other research where the polyphenol content varies between 3g/l and up to 9g/l [21]. Indeed, in addition to the fruit variety and climatic conditions, the phenolic composition of the margins also depends on the separation techniques used to separate the oil phase from the water phase that results in the margins.

**2. Results of Clay Geotechnical Analysis**

**2-1. Granulometric Analysis**

The results of the sieve analysis are presented in figure 10:

**Fig.10**: Particle size curve of natural clay

It is concluded that the sample studied contains a large variety of particles size.

**2-2. Atterberg Limits**

The Atterberg limit results are given in table 2:

|  |  |  |
| --- | --- | --- |
| IP (%) | Plasticity limit Wp (%) | Liquidity limit Wl (%) |
| 18 | 20 | 38 |

**Table 2**: Atterberg limit of natural clay

From the results of the liquid limit, we notice that the clay studied has a medium plasticity, while its plasticity index shows a clayey silt type.

**2-3. Sand Equivalents at 10% of Fine**

The sand equivalent study gave that:

ES = h1/h2\* 100 (%) = 28%

We deduced that the sample studied is clayey sand.

**2-4. Bulk and Apparent Density (Porosity)**

The apparent density and the bulk density allow us to calculate the porosity of the sample as follows:

n= 1- (ρapp)/ (ρbulk) = 15%.

**3. Characterisation of Manufactured Bricks**

The quality of bricks was determined by carrying out test series on the manufactured brick specimens, namely: porosity, bulk density, linear drying, firing shrinkage, mass shrinkage, absorption, and the brick compressive strength test.

**3-1. Porosity**

Figure 11 shows the evolution of the porosity of the cylindrical brick samples according to the percentage of substitution of the margins and according to the region where the margins samples were taken. The substitution of 10%, 20%, 30%, gives respectively 28.27%, 19.62%, and 18.5% (for the case of Ksar el Kebir) knowing that the control sample gives 32.7%. This decrease in pores is due, on the one hand, to the presence of phenolic acids of the margins which are characterized by an acid pH higher than 4.5, the phenolic acids are in ionized form, so they are easily retained on the surface of the clay, and, on the other hand, the clays contain strongly hydrated exchangeable cations (Ca2+, Mg2+) which allows to easily absorb the very soluble organic compounds of the margins (Cl-).

**The porosity in%**

**Fig.11**: Porosity of the studied bricks

**3-2. Absorption of Fired Bricks**

This factor is important in the manufacture of bricks as it determines their durability and is proportional to the porosity: absorption increases with increasing porosity. The results are given in figure 12.

**%Absorption in**

**Fig. 12**: Absorption of the studied bricks

**3-3. The Apparent Density**

The density of a clay brick is an important parameter, the results obtained in these tests presented in (figure 13), show that its value increases proportionally with the increase of the percentage of substitution, and inversely proportional with the increase in porosity such that the density increases with the decrease in porosity.

**Apparent density g/cm3**

**Fig. 13** Apparent density of the studied bricks

**3-4. Compressive Strength**

Compressive strength is the most important parameter in the manufacture of bricks. Figure 14 shows the variation of strength as a function of the percentage of margins substitution and according to the region of margins sampling.

**Compressive strength in MPa**

**Fig. 14:** Representation of the compressive strength of bricks

From these results we notice that the compressive strength is necessarily influenced by the increase of the substitution percentage of the margins as well as by the nature of these margins, whereas the strength is inversely proportional to the porosity.

**CONCLUSION**

The margins playing the role of liquid in this manufacturing process were introduced by substituting water with the percentages of 10, 20 and 30% of this oleic product. To ensure the results, studies were carried out on three types of margins from three different regions of Morocco.

The most important parameters influencing the quality of the bricks were studied such as compressive strength and porosity.

On the one hand, we notice that the strength increases with the rate of substitution for the same site and on the other, hand the strength increases correlatively with the increase of the concentrations of polyphenols and chlorides in the margins.

This relativity is reversed for the porosity which decreases with the increase of the concentrations and the substitution rate, which can be explained by the presence of phenolic acids which are strongly attached to the surface of the clays to fill the vacant sites of the external surface, as well as the presence of the very soluble organic compounds of the margins (Cl-) which react with the strongly hydrated exchangeable cations (Ca2+, Mg2+) of the clays to fill their internal surface sites.

Similarly, the absorption and bulk density results are consistent with porosity.

From a product quality point of view, the experimental results obtained are very encouraging (increase in the strength of the bricks obtained compared to standard bricks), and from an environmental point of view we can eliminate a large quantity of margins and subsequently reduce their harmful effects on the environment.

Finally, it is essential for our study to be complete to conduct thermal studies in order to observe the behaviour of bricks made from portions of margins.

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