

Two Phases olive mil residue composting – Chemical changes during the process

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Abstract: Olive oil production in the Mediterranean basin generates huge amounts of potentially polluting organic waste, namely olive-waste cakes, which urges to be economically and environmentally viable. Among the possible valuations of this residue its use as an organic fertilizer is particularly important for the poor Mediterranean soils. However, because of its composition, the direct use of this waste is impracticable especially in annual crops and must undergo a composting process before being utilized. It was with the objective to follow the difficult composting process of this residue, and the changes of its composition throughout this process, that we developed this study. To this end, after characterizing the residue to be composted and having decided to mix straw as a structuring product in order to facilitate the development of the aerobic biological transformation process, we established a static pile with mechanical stirring and manual humidification, weekly controlling the evolution of the composition of the residue during the composting process. The results show the lowering of the C/N and C/P ratios and a significant content decrease in phenols and polyphenols. As a conclusion we state that the process of composting, that we have developed, is valid to transform this residue into organic fertilizer, free of phytotoxicity, rich in humid organic matter and with a considerable macronutrient content that can be used economically and that it is environmentally adequate for the fertilization of agricultural soils.

Key Words: olive-waste cakes, composting, fertilizer, organic, residue.

1. Introduction

With an enormous territorial projection, olive grove cultivation and its productions, olive oil and table olives are considered staple foods in the Mediterranean diet due to its economic, social and environmental importance [1, 2]. According to the latest data from the International Olive oil Council (IOC), the world production of olive oil in 2017/2018 increased 14%, when compared to the previous campaign, reaching 2,894,000 Mg. According to the IOC, olive oil consumption for 2017/2018 will increase 5% to a total of 2,954.00 Mg. Considering that merely an average of 20% of the total olive weight entering the mill will be olive oil (depending on the olive variety, maturity stage, weather conditions during the olive growing stage, extraction of olive oil methodology, etc.), we can easily conclude that the annual production of olive oil indicated for 2017/2018 corresponds to something like 14,470,000 Mg of potentially pollutant organic waste, to which there must be some economically and environmentally destination.

Methods for obtaining olive oil have undergone several changes throughout history [3]. Thus, from the traditional mills, with pressing system working

discontinuously that required more labor and produced more acidic oil technology evolved to continuous systems. These new systems have the possibility to carry out a continuous process of obtaining olive oil, with a reduction of costs, mainly in the labor force, and a smaller environmental impact because they do not lead to the production of the so-called *águas ruças* (residual waters). In this process only a liquid phase, the oil, is obtained and a solid phase, commonly referred to as olive-waste cake [3].

The final destination of this organic waste remains a huge problem for the olive sector [4]. Recent research in the United States questions the sustainability and "ecology" of the use of these wastes in the production of biofuels, indicating that the energy balance of the process is negative. Incineration, while with advantages such as energy production, also entails a number of drawbacks, including gas emissions (amount of CO₂ released), generation of dioxins and furans during combustion and the dispersion of dust and acid oxides, causing serious impacts both in the atmosphere and in soil and water [5]. Thus, the olive sector presents increasing difficulties in the valorization of the waste that it produces, being forced to look for alternative methods for the management and treatment of mill

wastes [4]. On the other hand, Mediterranean soils are characterized by their low fertility and sustainability, mainly derived of their very low organic matter content [6]. One of the most effective solutions to the problems raised is to incorporate organic matter into the soil in order to increase the aggregation level of its particles, the permeability and water and nutrient retention capacity [6]. For this reason, the use of organic waste such as manure, is capable of improving the physical and chemical fertilization of soils. Nowadays, as an alternative to the scarcity of traditional manure, we started considering the use of organic waste from agri-food industries, from urban solid waste, sewage sludge, etc [7]. It is in this context that the use of residues of the olive industry as an agricultural fertilizer, either directly or after composting, presents itself as particularly relevant, achieving obvious improvements in physical, chemical and biological fertility of these soils [6].

2. Problem Formulation

The use of olive-waste cakes in nature presents, as we have mentioned, toxicity problems that may prevent the normal development of crops, and it is also considered a product with strong germination inhibiting properties due to its high content of phenols and polyphenols. In this way, composting appears as a process capable of attenuating this phytotoxic effect and providing this organic residue with more adequate characteristics to its use as an organic fertilizer in the agricultural activity [8]. However, the process of composting this residue is difficult and time consuming, with many changes occurring in the composition of this residue during the aerobic biological transformation process that we have been referring to [9]. It is with the objective of studying the optimization of the composting process and of analyzing the deep changes in its composition that olive-waste cakes undergo during the composting process that we carry out this study [9].

3. Material and Methods

3.1 Materials

3.1.2 olive-waste cake

The olive-waste cake (15 Mg) derives from an olive mill that uses the continuous two-phase centrifugation process (table 1). Before its analysis, it is dried in an oven at a temperature of approximately 50°C until reaching constant weight. Once dried, the olive-waste cake is milled in an electric knife mill and screened in sieves with a 0.5 mm pore diameter and subsequently homogenized. The homogenized samples are stored in tightly sealed polyethylene containers.

3.1.2 Structuring materials

In this study we used wheat straw (3 Mg) from a producer in the region (Table 1).

3.2 Methods

The composting method consisted in the formation of stationary piles with mechanical stirring, due to the simplicity, low cost and good quality demonstrated in the formation of the compound, using a wide variety of materials.

The pile components mixture was carried out layer by layer alternating the olive-waste cake with the structuring material, taking special care after the addition of each layer in order to obtain the most homogenized mixture possible. The prepared pile had a trapezoidal shape, approximately 3.5m in size and about 1.5m in height.

Table 1- Chemical composition of the Two phases olive mil residue and wheat straw.

Parameter	Units	Two Phases olive mil residue	Wheat straw
Humidity	%	64.2	2.89
pH		5.49	7.23
CE	dS m ⁻¹	3.73	9.17
Org. matter	%	91.22	88.2
Lenhine	%	19.6	3.87
Hemicellulose	%	19.1	33.21
Cellulose	%	22.8	42.06
Polifenols	g kg ⁻¹	7.3	6.05
N	% N	1.79	0.68
P	% P	0.18	0.08
K	% K ₂ O	2.75	1.97
Ca	% Ca	0.48	0.30
Mg	% Mg	1.29	0.22
Fe	mg Kg ⁻¹	1424	777
Cu	mg Kg ⁻¹	24	6
Zn	mg Kg ⁻¹	19	7
Mn	mg Kg ⁻¹	71	38

The process took place over a five-month period. Periodically the piles (composition of the water used in Table 2) were carried out, vented and watered in order to preserve adequate conditions of aeration and humidity. In addition, periodic samples were collected throughout the process for further analysis. (Table 3). The irrigation was periodic throughout the process, more frequent at first, but realized as needed, whenever the percentage of humidity of the piles was less than 50% and always adapting to the needs of the process.

Table 2 – Chemical composition of the water used

Parameter	Units	Water composition
pH		7.2
CE	dS m ⁻¹	0.79
Ca	mg L ⁻¹	116
Mg	mg L ⁻¹	31
Na	mg L ⁻¹	17
B	mg L ⁻¹	0.24
SAR		0.36
NO ₃ ⁻	mg L ⁻¹	16.7
Cl ⁻	mg L ⁻¹	28.4
HCO ₃ ⁻	mg L ⁻¹	347.1
Dureza	mg L ⁻¹	417.4

Table 3 – Dates of the main proceedings during the process

Dates of Reversing	Dates of Irrigation	Amount of water used (Liters)	Dates of sampling
22 Jan	26 Jan	300	8 Jan
9 Feb	5 Feb	300	22 Jan
23 Feb	12 Feb	400	5 Feb
2 Mar	20 Feb	300	19 Feb
22 Mar	28 Feb	700	5 Mar
6 Apr	3 Mar	400	19 Mar
20 Apr	8 Mar	300	29 Mar
30 Apr	15 Mar	500	2 Apr
4 May	22 Mar	500	16 Apr
11 May	29 Mar	500	30 Apr
28 May	6 Apr	500	7 May
	20 Apr	200	14 May
	2 May	100	21 May

3.2.1 Sampling and analytical methods

Samples were periodically collected (Table 3) by harvesting four subsamples of approximately 1,000g around the pile. They were removed at 80cm high, making a cross section, and scraping the outside of the sample. The samples were then dried, crushed with 4 mm stainless steel sieve and ground for further analysis [10].

Moisture - Determined gravimetrically after keeping the sample in an oven at a dryness temperature of 105°C, until constant weight was reached [10];

Temperature - This parameter was monitored daily inside the pile using a digital thermometer connected to a temperature probe (model Crison 638) of 1m in length. The probe was introduced at approximately 1m in a height of 0.5m. This process was repeated in four different points, in the contour of the pile, finally obtaining its arithmetic mean [10]; **pH** - Determined on a mixture of residue suspension and water in a 1:5 ratio (MAPA, 1994). The measurement was carried out with the aid of a pH-meter Crison-501 with glass electrode [10]; **Conductivity** - Determined on a mixture of residue and water in a ratio of 1:5 (v/v) with a Conductivity Meter Chryson 522, supplied with

conductivity cell $c = 0.99$ [10]; **Organic Matter** - Determined by weight loss by calcination. Once the material is dried, it is burned for 4 hours in a muffle at a temperature of 600°C. By weight difference, the percentage of organic matter was obtained [10]; **Total nitrogen** – we used the Kjeldahl method consisting in the transformation of the organic nitrogen into ammoniacal by digestion of the sample with sulfuric acid, potassium sulfate, copper (II) sulphate and selenium. In a second step, the ammonia formed is distilled in basic medium by the vapor trap, collecting the distillate in a solution of boric acid indicator. Subsequently, ammonia is determined by acid titration of the ammonium borate formed [10]; **Phosphorus** - was extracted by digestion with 50% HCl and then determined by titration of the formed complex of phosphomolybdate by spectrophotometry at 400 nm of wavelength [10];

4. Results and Discussion

4.1. Temperature

The following figure (Figure 1) shows the temperature evolution during the composting period of the test pile.

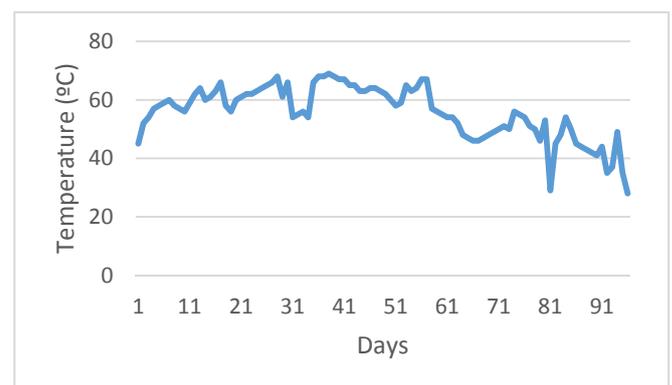


Figure 1: Compost pile temperature over the study period

Temperature is a fundamental parameter throughout the process, as it will be the main indicator of its evolution. In general, a thermophilic stage is followed by a mesophyll one and a third mesophyll stage before the maturation stage, where the organic matter begins to acquire the typical characteristics of the compound. The tested pile fulfills the temperature conditions necessary to obtain a pathogen free compound (reaching temperatures of 60 °C or higher for several days) [11].

4.2. Humidity

In the moisture evolution (Figure 2) we observed that, during almost the whole process, the pile maintained a constant 50 - 60% humidity which is the mark considered as being great for a correct activity of microorganisms [11].

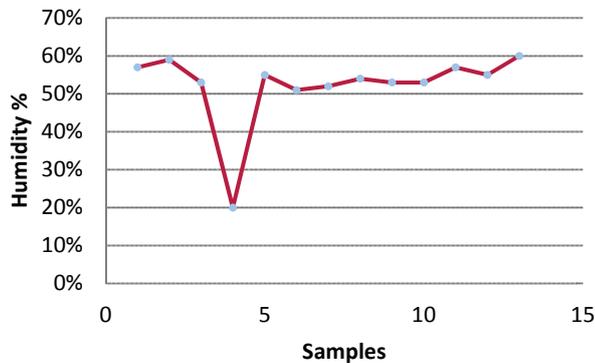


Figure 2: Humidity variation during the development of the composting process

Several authors have shown that the biological activity decreases considerably when the humidity drops by 30% or exceeds 70%. Maintaining optimum moisture levels is of the utmost importance to provide a good composting process, preventing leachate excess [11].

4.3. Conductivity

High salt content may directly affect seed germination and overall crop development. Therefore, the electrical conductivity (CE), should be controlled in the composting processes.

Carbon values fluctuate slightly during the course of the composting and decrease significantly in the final phase of the process (Figure 3). The justification for this result is salt release, the degradation of organic matter and the irrigation carried out which together will be responsible for the elimination of the soluble salts. The final C values obtained in our study are lower than those found by other authors in composting of olive-waste cakes [5].

The EC values obtained in the final products of the tested treatment ensured that their use, as a corrective or organic fertilizer, does not represent any risk of salinization to the soils that receive them.

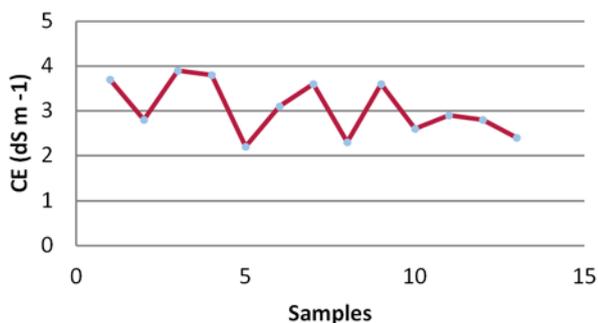


Figure 3: variation of Electric Conductivity during the composting process development

4.4. pH

As stated in Figure 4, except for the initial phase where there is a small decrease in the values of this parameter,

which can be due to the release of organic acids from the decomposition of organic fractions of the residue, pH increases during the remaining period of composting. In a similar study, [5] found higher pH values, possibly due to the fact that its main structuring agent are pastures, not straw, as in this case.

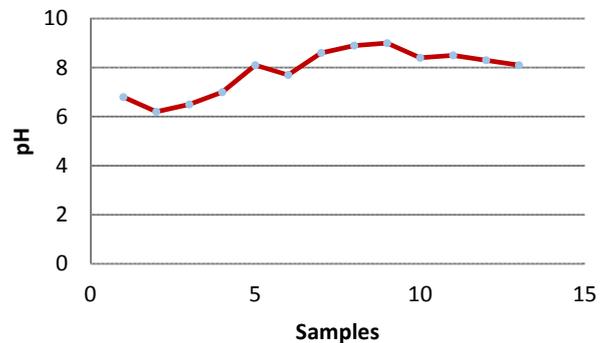


Figure 4: pH variation during the development of the composting process

4.5. Organic matter

The organic matter values decrease throughout the process (Figure 5) and an identical result was obtained by [12].

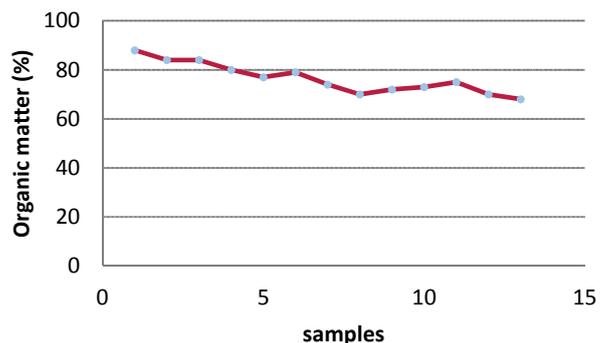


Figure 5: Organic matter content during the development of the composting process

Organic matter degradation from the residue occurs with more intensity in the first four months, coinciding with the thermophilic phase and, from there, with the development of the mesophyll phase, the content of organic matter in the residue in compost tends to stabilize.

4.6. Total Nitrogen

The total N content of the compound is a direct function of the starting materials, the composting process and the maturation and storage conditions.

The total nitrogen values undergo a considerable increase from about 1.8% initial value to 2.8% obtained at the end of the process. There is a gradual rise over the

first 4 months and then the contents remain more or less constant until the end of the process. This can be explained by a concentration effect caused by the intense biodegradation of organic compounds that were not nitrogenous [5, 13]

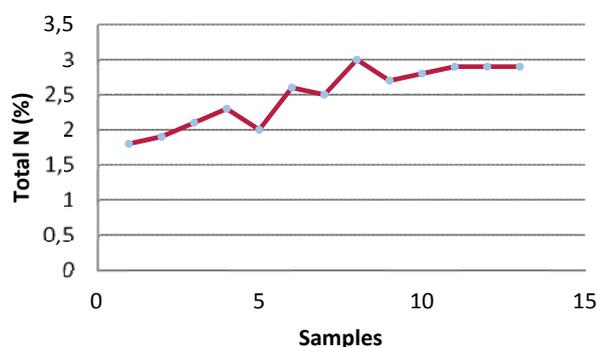


Figure 6: Total Nitrogen content variation during the development of the composting process

4.7. Phosphorus

Phosphorus is the most important nutrient, after C and N, so it must also be present in adequate quantities for the composting process to be carried out correctly.

As shown in Figure 7, from the second month on, the content of P undergoes a clear rise, reaching values close to 0.9%, results much higher than those obtained by [14].

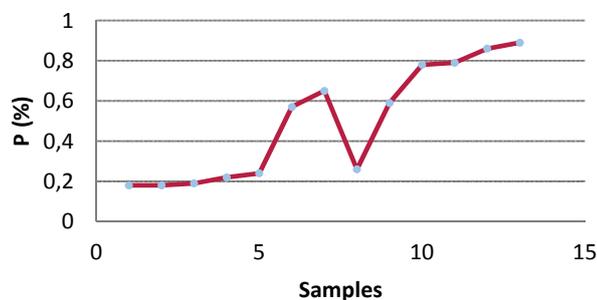


Figure 7: Phosphorus content variation during the development of the composting process

It should be noted that, in the final product, P level is below the limit quantity that enables it to be cataloged in the good quality compound (0.5%).

5. Conclusions

The utilized olive-waste cakes have an optimum C/N ratio to ensure adequate nitrogen release if the residue is directly applied without composting. On the other hand, its low phosphorus content conditions the C/P ratio and leads to it being much higher than the optimal limit, so that a serious immobilization of this element

would be expected if the residue were applied without previous composting.

The temperature reached during the composting process is shown to be suitable for the destruction of any existing pathogens.

The values of EC obtained at the end of the composting process indicate that the use of this compound as organic fertilizer does not bring any risk of salinization to the soil.

The pH values obtained at the end of the process lead us to characterize this compound as slightly alkaline and therefore particularly suitable for use in acidic soils, which are largely dominant in the Mediterranean basin. During the composting process the organic matter content decreases. In turn, this degradation does not exceed 20%, obtaining final values of 70%, much higher than the 25% established as suitable for quality compounds.

The concentration effect caused by the intense biodegradation of non-nitrogenous organic compounds causes the total nitrogen concentration to rise considerably, reaching values of 2.8%.

The natural concentration of nutrients, due to weight losses of material that occurs in compost piles, leads to a strong increase of phosphorus levels in the final compound, reaching values close to 2%, much higher than the 0.5% established as the limit in order for it to be cataloged as a quality composite.

Acknowledgments: The authors would like to acknowledge the support given to the authors through the project 0049_INNOACE_4_E open and smart innovation in EUROACE co-financed by the European Regional Development Fund (ERDF) under the INTERREG V - A Spain-Portugal (POCTEP) 2014-2020 program.

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