Olive stone wooden residues and olive pomace characterization - potential uses in co-composting with olive mill wastewater

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Abstract
Co-composting of the solid residues and wastewater from the olive oil production process was examined as a potential bioremediation treatment for these wastes. Experimental results from a laboratory pilot plant were reported. Composting temperature ranged from 55 to 72 ^{o}C and oxygen partial pressure from 10 to 17%. An operational region of temperature and oxygen partial pressure was defined in order to achieve a ratio of olive mill wastewater consumption to olive stone wooden residue stabilization equal or greater than 2.5, the typical ratio for an olive mill plant. Another critical parameter for the optimisation of the co-composting process that was examined was the biological efficiency of the process. A strong sigmoid correlation of co-composting efficiency with temperature derived, reaching a maximum plateau of 0.50 at 68^{o}C. The optimum conditions proved to be 68^{o}C and 16-17% oxygen partial pressure, rendering the co-composting process an integrated treatment scheme for olive mills.
Keywords: Aeration rate; Co-composting; Olive mill wastewater; Olive stone wooden residues; Temperature effect

Introduction
Mediterranean countries produce 97% of the total olive oil production, while European Union (EU) countries produce 80–84%. The biggest olive oil-producing country is Spain, then Italy, Greece and Turkey, followed by Tunisia, Portugal, Morocco and Algeria (Paraskeva and Diamadopoulos 2006).

Olive mill wastewater (OMWW) arises from the production of olive oil in olive mills. It is produced seasonally by a large number of small olive mills scattered throughout the olive oil-producing countries. OMWW has a very high organic load, recalcitrant in nature and with a high amount of toxicity/phytotoxicity-associated compounds. Several physicochemical, biological and combined processes have been examined for the treatment of OMWW, resulting in considerable organic load and toxicity abatement. Biological processes, aerobic and anaerobic, including anaerobic co-digestion with other effluents and composting, are predominant in the treatment of OMWW. Advanced oxidation processes have attracted much attention due to the strong oxidation potential of the agents used. Although the problem of OMWW treatment could be more or less solved technologically, it is still far from being solved realistically, mainly because of practical/economical reasons. Owing to the small scale and dispersed nature of the olive mills and the seasonality of the process, affordable solutions have not yet yielded the required quality to meet stringent environmental standards (Paraskeva and Diamadopoulos 2006).

Apart from high strength wastewater, during olive oil extraction process solid residues derive. The final by-product of the olive oil production process is the olive stone wooden residue (OSWR). For every kg of olive processed, 0.25 kg of OSWR are produced. The calorific value of OSWR is about 4500 kcal/kg and it is usually used as a fuel in greenhouses, ceramic and lime production plants, bakeries as well as in the olive mills and seed oil mills (Taralas and Kontominas 2006). Recently, the demand of OSWR is decreasing despite the fact that it is cheaper compared to fuel oil. This can be attributed to the fact that OSWR is more difficult to handle, transport, store and burn (Vlyssides et al. 1999). Unpleasant odours are emitted during its storage due to possible anaerobic conditions, thus restricting its use. Furthermore, strict environmental legislation on biomass incineration sets another obstacle on OSWR burning. Consequently, at least 25% of the produced solid residues remain unused and hence new uses of this biomass are sought (Vlyssides et al. 2008).

This paper proposes an integrated method for the treatment of olive mill wastewater and olive stone wooden residues by co-composting. Composting is an aerobic procedure for organic solid waste stabilization. During the composting the easy biodegradable organic matter, under exothermic aerobic bioreactions, is stabilized producing biomass, carbon dioxide and thermal energy (Kaiser 1996; Paraskeva and Diamadopoulos 2006). The produced thermal energy is able to increase the temperature up to almost 80^oC depending on the total heat transfer coefficient of the bioreactor and on the easy biodegradable fraction of the substrate (Mason and Milke 2005). As the temperature rises, the bioreaction rates are increased. In order to keep temperature around the optimum thermophilic range of 60-70^oC, air is supplied as a cooling mean (Vlyssides et al. 1996). The applied air also transfers the proper amounts of oxygen for the biological respiration needs. Generally the amount of air that must be supplied for cooling purposes in a composting system is about nine times greater than that for respiration needs. So the air for cooling needs is the controlling parameter for oxygen supply. Other parameters that control the composting procedure are: the temperature of the process, the moisture of the bulking material and the nutrients (nitrogen and phosphorous) (Haug 1980). Also the homogenization of substrate, moisture and temperature is another important parameter for a more effective composting because under non-uniform conditions, different cultures that are usually competitive are grown, thus interrupting the degradation process. For a continuous and stable process, the removed carbon by degradation as well as the moisture removed by evaporation must be replaced (Kaiser 1996). In this paper the OSWR were used as substrate (bulking material) and the OMWW as a supplier of moisture, carbon and nutrients. The concept of this approach is based on the continuous replacement of the aerobically digested organic carbon and the evaporated moisture, that are lost during the composting of the organic solid material, by the organic carbon and water content of the wastewater respectively. In a typical olive mill plant the ratio of OMWW to OSWR is approximately 2,5. Thus, the aim of this paper is to specify such operational conditions of co-composting process that would result in a ratio of olive mill wastewater consumption to olive stone wooden residue stabilization equal or greater than 2,5. The biological efficiency of this process is also set under investigation.

Materials and Methods

Apparatus: In order to examine the feasibility of the proposed method a fully computerised laboratory apparatus was designed and constructed (Figure 1). The critical parameters for the growth of microorganisms and bioreactions during co-composting are the oxygen demand, the moisture and the temperature.

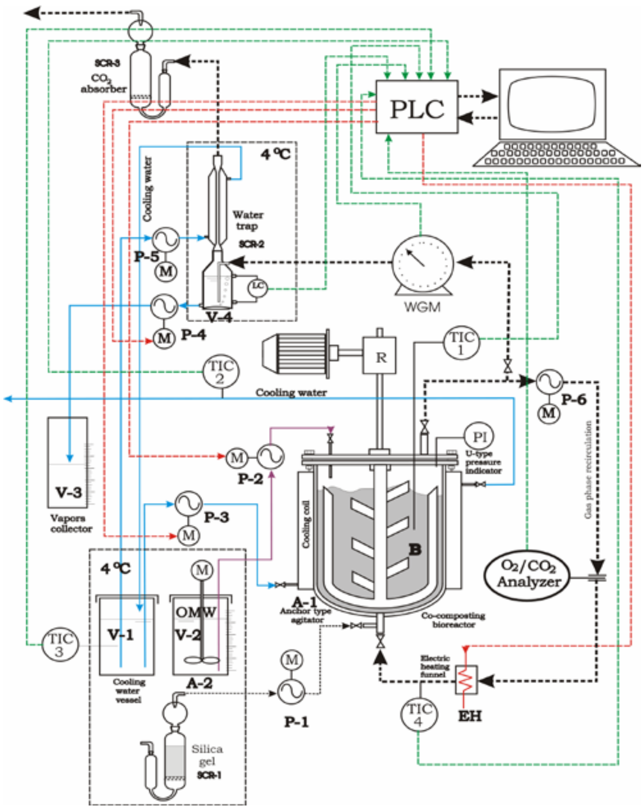

Fig.1: Experimental apparatus of co-composting

The composter (B) consists of a cylindrical double layered metal autoclave of 22 cm internal diameter and 28 cm height (10.058 L active volume) with a six wing anchor agitator. The wastewater is stored in a refrigerator (4^{o}C) in order to avoid any undesirable biological degradation.. The feeding of the wastewater through the stirred storage vessel V-2 is achieved by the peristaltic pump P-2. The wastewater is added in the bioreactor in order to maintain constant the moisture of the system. The parameters that are taken into consideration for wastewater addition are: the moisture that is lost with the evaporating gases, the OSWR hydrolysis rate as well as the water produced from the biological reactions..

The gas phase homogenization is achieved by continuous gas recycling through a peristaltic pump (P-6). A O_2/CO_2 gas analyzer is included in the gas-recycling line. During the bioreactions, oxygen is consumed and carbon dioxide is produced, thus the oxygen partial pressure tends to lower. The control of this parameter is performed by feeding dry atmospheric air according to the O_2/CO_2 gas analyzer's indications. When air is fed to the system, its pressure is increased. When the pressure exceeds the pressure of the water column in V-4 (20 cm H_2O), gases move from the bioreactor to V-4 passing through a Wet Gas Meter (WGM). The moisture of this gas phase is removed by a water trap SCR-2. The level controller (LC) is used in order to maintain the pressure of V-4 constant and thus the excess moisture is collected in V-3. Through this simple and fully handlable system the bioreactor may operate under constant pressure.

The temperature inside the bioreactor is monitored by the TIC-1 and fully controlled. The heating of the reactor is achieved by the heating of the recycled gas through an electric resistance (EH). The latter is set in operation when the temperature indicated by TIC-1 is below the set point. The temperature of the recycled air cannot be over 80^{o}C thus it is checked by TIC-4. The bioreactor's cooling is achieved by circulation of cool (4^{o}C) water between the layers of the reactor. The cooling water is fed by P-3 pump.

Raw materials

Olive stone wooden residue: Olive stone wooden residue (OSWR) was used as bulking material for the co-composting process. The OSWR samples were taken from an olive mill plant in Crete, Greece. It is worth mentioning that the solid residues composition varies from area to area and from year to year depending on the climatological conditions, cultivation etc. The main physical and chemical characteristics of the OSWR used are presented in Table 1. The solid residues were classified by sieving.

Olive mill wastewater: The water needs of co-composting process were fulfilled by olive mill wastewater (OMWW) produced in the same olive mill plant in Crete, Greece. The composition of the OMWW used for all experiments is shown in Table 2.

Experimental procedure: The experiments were conducted in a semi-batch mode; the OSWR was loaded in the beginning of each experiment and the addition of wastewater was performed according the water needs. In each experiment, the temperature, oxygen partial pressure and moisture were kept constant to a predetermined set point. It was possible to fully control these parameters due to the appropriate design of the apparatus and its automations. During the experiments various parameters were continuously recorded. Parameters such as wastewater addition, effluent gas flow rate and composition and energy needs may give useful information for the progress of co-composting process. The critical parameters for the optimisation of the co-composting process are the ratio of the wastewater addition to the wooden residue consumption and the efficiency of the co-composting process. The term efficiency of co-composting process is defined as the carbon dioxide produced by the biological reactions to the total carbon available (both from wastewater and bulking material) to the microorganisms.

In this context, an experimental plan was designed. The parameters that were examined were: Temperature ranging from 55 to 72 ^{o}C and oxygen partial pressure ranging from 10 to 17%. The moisture was kept constant at 40%. 8 series of experiments were conducted under constant oxygen partial pressure (10 to 17%, step 1%) and temperatures 55, 58, 60, 62, 65, 68, 70, 72 ^{o}C. The end of each experiment was set at 20 d (480 h). At the end of each experiment the bulking material (OSWR) was dried, weighed and classified.

Results and discussion: During the 20d period of each experiment, the carbon dioxide produced and wastewater added was recorded on an hourly basis. For example, the results that derived during the experiment conducted under 65^{o}C and 12% oxygen partial pressure are presented in Figures 2 and 3. Figure 4 illustrates the variation of the weight distribution of the bulking material at the beginning and at the end of the experiment. It is obvious that by the progress of co-composting the curve was displaced to lower diameters resulting in a total weight decrease. This was the case for all experiments. The final product - compost that was produced after a two-month maturation period had the characteristics presented in Table 3. From the processing of the experimental results, in this case, the ratio of total wastewater added to the olive stone wooden residue loss was calculated equal to 1.47 and the corresponding co-composting efficiency 0.45.

Figure 5 presents the correlation of the OMWW/OSWR ratio with oxygen partial pressure under different constant temperatures. It is evident that there are strong exponential correlations between the parameters mentioned above. These correlations are presented in Table 4.

Figure 6 presents the influence of both temperature and oxygen partial pressure on the OMWW/OSWR ratio. Taking into consideration the fact that the ratio of olive mill wastewater to olive stone wooden residue produced in a typical olive mill is approximately 2.5, an operational region of the co-composting process could be defined (Figure 6).

Figure 7 presents the correlation of the co-composting efficiency with temperature under different constant oxygen partial pressures. It is obvious that these curves follow a sigmoid pattern and that the co-composting efficiency is almost independent of pressure. The sigmoid correlation (R^2=0.9959) that best fitted these results is the following:

$$\text{co} - \text{composting efficiency} = 0.18579 - \frac{0.30673}{1 + 10^{20.9411 - 0.32891 \cdot T}}$$

Based on the equation above as well as Figure 7, the co-composting efficiency reaches a maximum plateau of approximately 0.50 at 68°C.

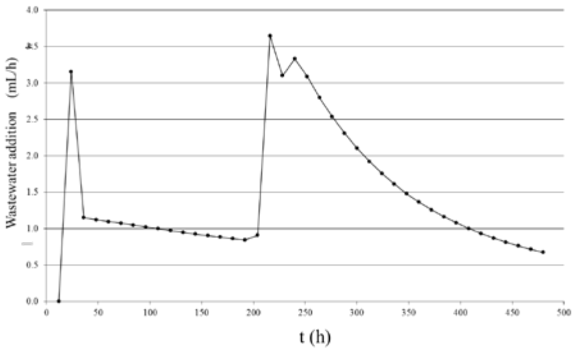

Fig. 2: Typical time variation of wastewater addition during co-composting at 65 °C, 12% oxygen partial pressure and 40% moisture

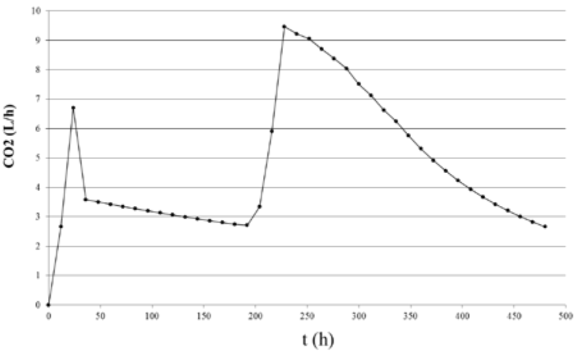

Fig. 3: Typical time variation of carbon dioxide production during co-composting at 65 °C, 12% oxygen partial pressure and 40% moisture

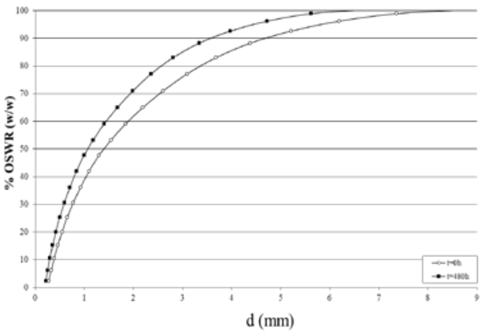

Fig. 4: % weight distribution of fractions with different particle diameters

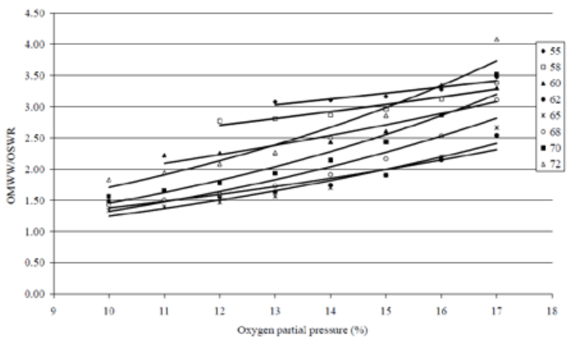

Fig. 5: Correlation of the OMWW/OSWR ratio with oxygen partial pressure under constant temperatures and 40% moisture

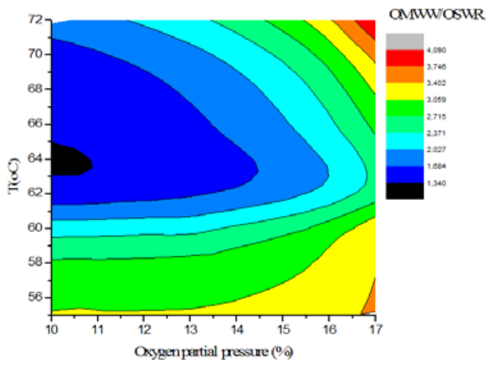

Fig. 6: Effect of temperature and oxygen partial pressure on the OMWW/OSWR ratio

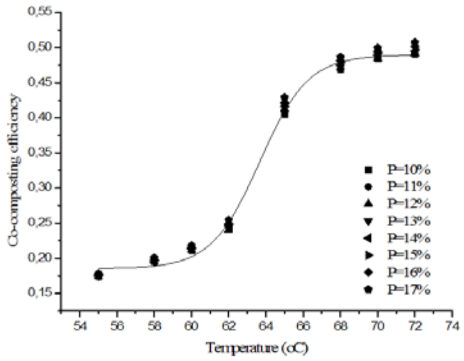

Fig. 7: Effect of temperature and oxygen partial pressure on the co-composting efficiency

Table 1. Physical and chemical characteristics of OSWR

Characteristics			
Moisture ,%	13,50	±	0,52
Fats and oils ,% of TS (total Solids)	1,85	±	0,69
Nitrogen content substances ,% of TS	7,39	±	0,037
Total sugars, % of TS	2,13	±	0,025
Cellulose, % of TS	37,39	±	0,438
Hemicellulose, % of TS	17,04	±	0,942
Ash, % of TS	3,66	±	0,225
Ether extraction substances, % of TS	8,61	±	0,035
Lignin, %of TS	21,97	±	0,45
Kjendahl Nitrogen content, % of TS	1,093	±	0,015
Phosphorous content as P_2O_5, % of TS	0,113	±	0,008
Potassium content as K_2O, % of TS	0,83	±	0,07
Calcium content as CaO, % of TS	0,95	±	0,092
Total Carbon content, % of TS	56,13	±	4,48
C/N ratio	51,34	±	4,52
C/P ratio	1137	±	99,11

Table 2: Composition of Olive Mill Wastewater (OMW) used in experiments.

Characteristics	**Value (mg L^{-1})**
pH	4.2
BOD_5	25850
COD	80250
Total Suspended Solids	4580
Volatile Suspended Solids	4024
Total Phosphorus	870
Total Kjeldahl Nitrogen	1150
Total Phenolic Compounds (TPC)	14250

Table 3. Final product characteristics

Parameter	Value (% dry basis)
Organic matter	60-85
Nitrogen	1-2
Phosphorous	0.035-0.065
Humic substances	5-15
Ash	15-40
Moisture	30-40

Table 4: Exponential equations correlating the OMWW/OSWR ratio with oxygen partial pressure (10-17%) under different constant temperatures and 40% moisture

Temperature, (°C)	Equation	Correlation coefficient R^2
55	$\frac{OMWW}{OSWR} = 2.0578e^{0.0298 \cdot P}$	0.9027
58	$\frac{OMWW}{OSWR} = 1.698e^{0.0388 \cdot P}$	0.9352
60	$\frac{OMWW}{OSWR} = 1.0275e^{0.0646 \cdot P}$	0.9199
62	$\frac{OMWW}{OSWR} = 0.6559e^{0.0741 \cdot P}$	0.9292
65	$\frac{OMWW}{OSWR} = 0.4841e^{0.0945 \cdot P}$	0.9355
68	$\frac{OMWW}{OSWR} = 0.449e^{0.108 \cdot P}$	0.9502
70	$\frac{OMWW}{OSWR} = 0.4695e^{0.1129 \cdot P}$	0.9568
72	$\frac{OMWW}{OSWR} = 0.5575e^{0.1119 \cdot P}$	0.9607

Conclusions

Taking into consideration all the experimental data mentioned above, it can be concluded that the method of co-composting can be successfully used in order to both consume the olive-mill wastewater as well as to stabilize the olive stone wooden residue. In other words the proposed technology achieves to treat successfully all wastes produced during olive oil production.

A sigmoid correlation of co-composting efficiency with temperature derived. This equation could be a useful tool for the estimation of an operational temperature for an efficient co-composting. It was proved that the efficiency of the co-composting process was independent of the oxygen partial pressure. This conclusion indicates that in the working system the oxygen was not the limiting factor for the biological reactions and thus the oxygen partial pressure does not influence the efficiency value. The supplied air apart from meeting the oxygen needs for the biological reactions, is necessary for cooling purposes and the enhancement of the wastewater evaporation, which is one of the main goals of this system. Given the sigmoid pattern of the curve, co-composting efficiency reaches its maximum value at 68°C. Any increase above this temperature does not result in a subsequent increase of efficiency, but simply to unnecessary energy cost. If the wastewater treatment is set as the first priority in this treatment scheme, then the ratio of the wastewater addition to the wooden residue consumption should be at least 2.5. Consequently, from Figure 6 a broad operational region of temperature and oxygen partial pressure was defined. In order to render co-composting an integrated treatment scheme for olive mill plants both parameters, OMWW/OSWR ratio and co-composting efficiency, should be taken under consideration. Thus, the optimum conditions proved to be 68^{o}C and 16-17% oxygen partial pressure.

Conclusively, the co-composting process could lead the olive oil production to sustainability, by producing a fertiliser ready to return to olive tree cultivations from the liquid and solid wastes of the production process.

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