Olive Mill WasteWater: From a major environmental issue to an eco-responsible valorisation.

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Olive oil industries generate large quantities of wastes around the Mediterranean. The three-phase system is an extraction process widely used in some countries (Italy, Greece, Tunisia, …) and it generates a liquid effluent named Olive Mill WasteWater (OMWW). This effluent is an aqueous waste (> 80% of water) containing organic compounds (fatty acids, …) and salts. The generated OMWW exceeds 8 million tons per year around the Mediterranean. Currently, this harmful effluent is generally discharged in open-air basins. The combination of sun heating and wind causes a rapid waste dewatering, which forms a crust (plastic consistency) that limits the mass transfer (limitation of water evaporation and oxygen diffusion). In these conditions, the fluid percolates into the soil and the lack of oxygen inhibits aerobic biological treatment. Soils become infertile and, groundwater as well as rivers can be polluted.

In this context, we have developed a strategy (Figure 1.) to recover this effluent for material and energy applications. enduring this strategy, the wastewater is impregnated into a biomass (sawdust, wood chips, olive solid residue, …), and then dried by a natural energy supplier (solar heater for example). The dry residue can then be used either for energetic purpose or as a long lasting soil builder, while the evaporated water is condensed and recovered for agricultural use (irrigation).

![Figure 1. Methodology proposed for OMWW valorisation](image)

The solid residue was previously recovered as an energy vector [1] and as soil amendment [2]. In the first case, the calorific value of the biomass is enhanced, providing an interesting and competitive green fuel. In the second case, a biochar is produced in order to be applied for soil amendment.

In this study, the main purpose is to recover the water during the drying step. Therefore, drying is performed in a laboratory convective dryer at the outlet of which a double-walled aluminium alloy condenser boiler is implemented. The hot and wet air is introduced in the condenser boiler, which is cooled by a circulating antifreeze fluid. The water is recovered for further analyses. The same experiments were performed with the biomass moistened in order to better understand the relative contributions of OMWW.

Main results include possible use of the recovered waters for irrigation purpose as they satisfy many countries standards for irrigation, namely electric conductivity, cations (Na+, Mg2+, Ca2+, K+, Ptotal, …), heavy metals, nitrates, chlorides and biological tests. Nevertheless, the pH of the recovered waters is in the range 3.5 – 4 while it should be between 6.5 and 8.5. Besides, the COD does not meet the acceptable values as they are 10 to 20 times higher.
In order to control the factors (organic compounds) that increased the COD and the acidity of the solutions, additional experiments were performed by Gas Chromatography and Mass Spectroscopy. Chemicals were identified by using NIST 05 database and validated by comparison with commercial standards. Comparison was also made between condensed waters of pure OMWW, impregnated OMWW and wet biomasses. As expected, the identified organic compounds were provided by OMWW. These compounds include mainly fatty acids (oleic, stearic, palmitic, hexadecanoic, myristic, pentanedoic, ... acids) and tyrosol, D-fructose, D-glucose, D-sorbitol. Other chemicals were found in recovered waters and came from the biomasses used (short-chain organic acids, L-phenylalanine, arabitol, myo-inositol, scyllo-inositol, ...). Among these organic compounds, some can be useful for plant growth (myo-inositol for example).

In order to meet irrigation standards, the water acidity and COD should be reduced. Two methodologies are tested (Table 1).

First, a filtration is carried out through coarsely crushed oyster shells (techniques used for pH rectification of drinking water). After rapid percolation of waters (2 or 3 seconds), the pH of the solutions was about 6 but the COD was still superior to the standard limit. To reach the irrigation standards, the water and the crushed shells (mass ratio 1g / 50 mL) needed to be in contact during about one minute.

Table 1. pH and COD after treatment for recovered water from OMWW and impregnated OMWW (sawdust) compared to minimum levels of standards for irrigation in Cyprus, Egypt, Italy, Morocco and Tunisia.

<table>
<thead>
<tr>
<th>Solution &quot;water from&quot;</th>
<th>Adsorbent</th>
<th>Contact time</th>
<th>pH</th>
<th>COD (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OMWW</td>
<td>Oyster shell</td>
<td>2-3 s</td>
<td>6</td>
<td>1.80</td>
</tr>
<tr>
<td>OMWW</td>
<td>Oyster shell</td>
<td>60 s</td>
<td>6.6</td>
<td>0.17</td>
</tr>
<tr>
<td>OMWW</td>
<td>Marble</td>
<td>2-3 s</td>
<td>6.8</td>
<td>0.12</td>
</tr>
<tr>
<td>Impregnated OMWW</td>
<td>Oyster shell</td>
<td>2-3 s</td>
<td>6.5</td>
<td>0.62</td>
</tr>
<tr>
<td>Impregnated OMWW</td>
<td>Oyster shell</td>
<td>60 s</td>
<td>6.6</td>
<td>0.08</td>
</tr>
<tr>
<td>Impregnated OMWW</td>
<td>Marble</td>
<td>2-3 s</td>
<td>6.8</td>
<td>0.08</td>
</tr>
</tbody>
</table>

The second test consists in a rapid percolation of condensed waters through marble powder coming from Tunisian open-pit mining. This powder is a solid waste that had so far no technical use, nor economic added value. After rapid percolation, the pH and the COD of the treated waters could meet the standards. The electrical conductivity and ion concentrations increased but were substantially below normal levels. In fact, the crushed cells and the marble powder have rectified the acidity of the solutions by releasing carbonate and bicarbonate ions. Moreover, fatty acids were adsorbed in bigger quantities and in shorter times, thereby reducing the COD of the solutions. The differences noticed with the two materials are probably due to the differences within the contact surfaces.

References
