BIOLOGICAL, ADVANCED OXIDATION & CHEMICAL TECHNOLOGIES FOR OLIVE MILL EFFLUENTS TREATMENT - A REVIEW

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ABSTRACT
The Olive Mill Effluent (OME) contains a high organic load, acidic pH and several recalcitrant and toxic substances, such as phenolic compounds and lipids hard to degrading. Due to this containing the OME cause a serious environmental descent, such as coloring of natural water, contamination of surface and ground waters, alterations in soil quality and odor nuisance. However different studies and research were carried out toward the development of efficient treatment technologies, to avoid theses environmental problems, including various physico-chemical and biological processes. Herein a brief review on the available worldwide olive mill effluent treatment processes used (Biological, Advanced oxidation and biochemical) processes.

Keywords: Olive Mill Effluents, OME, OMW, Biological Treatment.

I. INTRODUCTION
The foodstuff processing industry based on olive oil extraction and table olive preparation is an economically important activity for many Mediterranean sea countries, with Spain, Greece and Italy being the major producers [1-3]. This activity, however may represent a serious environmental problem due to the discharge of highly polluted effluents, the quantity of olive oil mill vegetation and the generated washing effluents (commonly referred to as olive mill effluents or wastewaters (OME or OMW)). Consequently the environmental impact, depends on the method of olive oil extraction used, the traditional cold press method typically generates about 50% of OME relative to the initial weight of the olives, while the continuous centrifugation process generates 80–110% of OME due to the continuous washing of the olive paste with warm water prior to oil separation from the paste. It is estimated that the annual OME production in the Mediterranean Sea region exceeds 30*10⁶ m³. OME may have COD values as high as about 220 g/l and the organic matter mainly consists of polysaccharides, sugars, polyphenols, polyalcohols, proteins, organic acids and oil [4]. Some of these substances are difficult to biodegrade and may exert toxic and inhibitory effects on the microbial activity [5, 6]. Moreover, OME contain considerable amounts of suspended solids that may reach up to 190 g/l [7]. It is estimated that every ton of milled olives corresponds to about 0.8 ton of OMW [8]. OMW usually contain COD values as high as 80-300 g/l and also considerable amounts of suspended solids [4].

So, the main concerns regarding the OME treatment are:

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OME are strong wastes containing high concentrations of phenolic compounds (up to 10 g/l depending on the type and origin of the effluent) that are difficult to biodegrade;
- Seasonal production which typically lasts between December and February and;
- Olive oil manufacturing industries are small plants with a daily OME flow rate between 10 and 100 m³ and are distributed over large areas.

OME treatment usually comprises a physico-chemical method aiming at the removal of organic matter from the liquid phase. This is usually done by means of lime coagulation [9], laboring for water evaporation and more recently membrane separation (i.e. reverse osmosis and ultrafiltration) [10]. These processes, however, suffer from serious drawbacks such as high cost, low efficiency and sludge-disposal problems [3]. Therefore, several degradation processes have gained a lot of attention as promising treatment technologies. The aim of this paper is to discuss recent research developments regarding the use of biological degradation and advanced oxidation technologies for OME treatment especially that traditional disposal on soil is still the typical solution adopted in Libya (for the region from Zliten to Garahbouli cities). Additionally in the recent years many studies have investigated on alternative treatment solutions more environmentally compatible than soil disposal.

II. BIOLOGICAL PROCESSES

There is no doubt that biological process is one of the most compatible and least expensive wastewater treatment methods. Anaerobic digestion is usually the basic biological process for OME treatment since it has many advantages compared to aerobic treatment. Where anaerobic processes required a lower intensive and produce lesser waste sludge than aerobic processes, in addition they may also be used for energy generation in the form of biogas. Furthermore they cope with seasonal OME production, since anaerobic digesters can be easily restarted even after several months of shutdown. However, both anaerobic and aerobic processes cannot cope with the high content of organic load of OME that need to be diluted several times prior to biological treatment, which lead to raising the cost of implications. This is more pronounced in the case of aerobic processes (dilution up to 70–100 times is often needed) that can operate efficiently only at feed COD concentrations in the order of 1 g/l. In addition to this, the presence of some classes of inhibitory and/or toxic compounds such as polyphenols and lipids render OME inappropriate for direct biological treatment [3, 9].

2.1. Aerobic Pretreatment

To enhance the anaerobic digestion of OME, an aerobic pretreatment stage may be favorable in reducing the amount of total phenolic compounds and associated toxicity. Borja et al. (1998) studied the effect of aerobic pretreatment using three different cultures (Aspergillus terreus, Azotobacter chroococcum, Geotrichum candidum) on the subsequent anaerobic digestion of OME and found out that the rate of anaerobic degradation was about 2.5–4.5 times greater (depending on the culture used) than that of the anaerobic degradation without pretreatment. This was attributed to the fact that pretreatment was capable of reducing the COD and total phenols concentration as well as toxicity by about 63–75%, 65–95% and 59–87%, respectively, for the various cultures used. In further studies, Fountoulakis et al. (2002) found that pretreatment of a thermally processed OME with Pleurotus ostreatus was capable of enhancing the performance of subsequent anaerobic digestion. Aerobic treatment for 21 days led to about 65% phenols removal, which was enough to remove inhibition against methanogenic bacteria. Several other studies have dealt with the efficiency of aerobic degradation concerning phenols and toxicity removal and representative literature is summarized in Table 1.
Table 1: Aerobic Treatment of OME

<table>
<thead>
<tr>
<th>Culture</th>
<th>Efficiency</th>
<th>Reference</th>
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<tbody>
<tr>
<td><em>Pleurotus ostreatus</em></td>
<td>Nearly complete removal of phenols after 20 days in batch fermenter. Phytotoxicity and toxicity to marine and soil bacteria were reduced following treatment. Toxicity to freshwater bacteria did not change.</td>
<td>[11]</td>
</tr>
<tr>
<td>Various strains of <em>Pleurotus</em></td>
<td>69–76% removal of phenols after 12–15 days in shake flasks. Phytotoxicity was reduced following treatment but not proportionately to phenols removal</td>
<td>[12]</td>
</tr>
<tr>
<td><em>Phanerochaete flavido-alba</em></td>
<td>70% color and 52% aromatic compounds removal after 14 days in batch fermenter</td>
<td>[13]</td>
</tr>
<tr>
<td><em>Phanerochaete chrysosporium,</em></td>
<td>92% phenols, 100% o-diphenols and 75% COD removal after 6 days with P. chrysosporium in batch fermenter. Respective values were 76%, 82% and 73% after 4.8 days with A. niger and 4%, 76% and 63% after 4.7 days with A. terreus. No phenols and only 10% o-diphenols removal after 9.3 days with G. candidum</td>
<td>[14]</td>
</tr>
<tr>
<td><em>Aspergillus niger,</em> <em>Aspergillus terreus,</em> <em>Geotrichum candidum</em></td>
<td>92% phenols, 100% o-diphenols and 75% COD removal after 6 days with P. chrysosporium in batch fermenter. Respective values were 76%, 82% and 73% after 4.8 days with A. niger and 4%, 76% and 63% after 4.7 days with A. terreus. No phenols and only 10% o-diphenols removal after 9.3 days with G. candidum</td>
<td>[14]</td>
</tr>
<tr>
<td>Various strains of <em>Penicillium</em></td>
<td>32–45% removal of phenols and 25–38% COD removal after 20 days in flasks.</td>
<td>[15]</td>
</tr>
<tr>
<td><em>Lentinula edodes</em></td>
<td>40% total phenols, 60% o-diphenols and 50% color removal with immobilized cultures in fixed bed reactor with recirculation. Toxicity to soil bacteria decreased following treatment</td>
<td>[16]</td>
</tr>
<tr>
<td><em>Azotobacter vinelandii</em></td>
<td>Elimination of phytotoxicity following treatment for 5 days in rotating biowheel Fermenter</td>
<td>[17]</td>
</tr>
<tr>
<td><em>Lentinula edodes</em></td>
<td>84% total phenols, 90% o-diphenols, 73% TOC and 75% color removal after 8 days with immobilized cultures in shake flasks</td>
<td>[18]</td>
</tr>
<tr>
<td><em>Coriolus versicolor,</em> <em>Funalia trogii</em></td>
<td>93% phenols, 81% color and 70% COD removal after 6 days with F. trogii in shake flasks. Respective values were 90%, 65% and 63% with C. versicolor.</td>
<td>[19]</td>
</tr>
</tbody>
</table>

2.2. Digestion with Other Effluents

Mixing and digesting OME with other effluents offers several advantages such as:
- Reduction of feed COD and total phenols concentration;
- No need to add nutrients (i.e. nitrogen and phosphorous) if OME are mixed with effluents rich in nutrients; and
- Possibility of running a year round treatment plant based on the co-digestion of seasonally generated effluents.

The concept has been demonstrated in recent studies by Marques [20] who studied the co-digestion of OME and piggery effluents (PE) (either raw or already anaerobically digested) in anaerobic filters. The process was capable of achieving 70–80% COD removal and 50–70% phenols removal at OME to PE volumetric feed ratios up to 83%. In further studies, Gavala et al. [21, 22] developed a mathematical model for the co-digestion of OME, PE and dairy effluents to predict the response of a digester subject to seasonal feed variations.

III. ADVANCED OXIDATION PROCESSES

Advanced oxidation processes (AOP) constitute a suitable treatment method for industrial effluents relying upon the intermediacy of chemical initiators (i.e. free radicals) and energy (i.e. heat) to destroy the target pollutants. Processes such as ozonation, Fenton oxidation, photocatalysis, electrochemical oxidation and wet air oxidation can only achieve partial decontamination even after prolonged treatment times. Given the specific treatment objectives, AOP may be used either for the complete mineralization of all pollutants to carbon dioxide, water and mineral salts or for the selective removal of the more bio-resistant pollutants and their conversion to biodegradable intermediates. The following AOP have been extensively studied in recent years; regarding their efficiency to treat OME;

3.1 Ozonation

Although ozone, a powerful oxidant, is not capable of completely treating highly concentrated OME since it is sparingly soluble in water. Several studies [23-26] have shown that the extent of COD removal achieved during OME ozonation even at the most favorable conditions could not exceed 20–30%. Nonetheless, ozonation may be used as a pretreatment method in a sequence of chemical and biological treatments [3].

3.2. Photocatalysis

A solar energy is a promising and cost effective method used for OME treatment considering that the major olive oil producing countries (such as Libya) benefit from high intensity solar irradiation throughout the year. The efficiency of the process has been demonstrated by Gernjak et al.[27], where OME were treated in various types of pilot-plant photo-reactors using solar light photocatalysis over TiO$_2$ or solar light coupled with Fenton. To enhance process efficiency, a pretreatment step such as flocculation and/or decantation was employed to remove suspended solids as they obstructed light from entering the liquid.

3.3. Fenton’s process

This process suitable to treat a wide variety of effluents irrespective of their origin and concentration. It is characterized by their simple and versatile operation. As olive oil manufacturing industries are usually small plants with a low, seasonal wastewater flow, a small Fenton unit would be sufficient to cope efficiently with the produced effluents. Rivas et al. [28] estimated that OMW treatment (15 g/l of inlet COD and 80–90% COD reduction achieved in residence times between 1 and 8 hr depending on the operating conditions employed) by Fenton’s reagent would cost USD 3.2/(m$^3$ of wastewater treated and g/l of COD removed). This value is greater than that of the conventional biological treatment of OME by about an order of magnitude since H$_2$O$_2$ consumption has a significant fraction on the operating costs. However further studies and evolutions are needed to obtain the optimum and economically dosage of the used Fenton’s components and avoiding waste of costly
chemicals, such as the study done by Rima et al. [29] which using a new system of oxidation which produces hydroxyl radicals through combination of zero valent iron and bubbling air into an acidic solution the main results were the generation of high concentrations of highly reactive Hydroxyl free radicals that leads to COD percent versus time in the OMW solution were found to decrease by about 99% after 50 min of treatment.

3.4. Electrochemical Oxidation

NaCl-assisted electrochemical oxidation offers a potentially cost-effective treatment process since OME can be destroyed through a combination of direct and indirect anodic oxidation; the latter occurs via the in-situ generation of powerful oxidants such as chlorine, hydroxyl radicals and oxygen. A drawback associated with the use of NaCl as the electrolyte is the likely formation of toxic organochlorinated by-products that need to be removed from the effluent prior to its disposal. Conversely, salinity of the treated effluent is not a problem if it is to be discharged in seawater [30, 31]. Alternatively, electrochemical oxidation may be coupled with another AOP such as the Fenton’s reagent to achieve improved removal rates (i.e. the electro-Fenton process), [32].

3.5. Wet Air Oxidation

High-temperature, high-pressure processes such as wet air oxidation can achieve high COD removals at relatively short treatment times. A major drawback is that wet air oxidation is usually an expensive process to install and operate because of the severe conditions required. High capital and operating costs are associated with the elevated pressures employed and the use of proper construction materials that should be resistant to the high corrosion rates occurring under severe operating conditions. In contrast, the cost associated with high temperatures is not a major concern as the process becomes thermally self-sustained with the organic load typically found in OME [32, 33].

IV. INTEGRATED OF AOP AND BIOLOGICAL TREATMENT OF OME

Coupling chemical and biological processes has received a lot of attention in recent years as a promising treatment alternative for effluents that are too toxic to treat by only biologically method. The underlying principle behind process integration is that a chemical pretreatment stage may be capable of converting most of the biorecalcitrant pollutants commonly found in industrial effluents to more readily biodegradable intermediates followed by a biological treatment step to convert these intermediates to biomass, biogas and water. Chemical pretreatment usually comprises a mild advanced oxidation process aiming at the partial rather than complete mineralization; consequently, treatment costs associated with this step are relatively small. Treatment of OME by a sequence of chemical and biological processes has been demonstrated in recent studies that are summarized in Table 2. The last column qualitatively shows the impact of the integrated process on the effectiveness of the overall system compared to controls. It can be seen that process integration generally enhances OME remediation. However, in some cases, an adverse effect has been observed since the chemical oxidation step may have led to the formation of intermediates that would have been more bio-recalcitrant or toxic than the original effluent. It should be pointed out that other types of integrated treatment in which a preceding biological step is followed by further chemical oxidation (i.e. biological → chemical or biological → chemical → biological) are plausible. Such integrated systems are particularly favorable for effluents such as OME that initially contain some biodegradable fractions (i.e. sugars and proteins) which could be easily removed first, and so subsequently would not compete for the chemical oxidant. This concept has been demonstrated by Benitez et al. [24] who compared OME treatment efficiencies for ozonation followed by
aerobic degradation, aerobic degradation followed by ozonation, ozonation alone and aerobic degradation alone. Overall COD removals of 81.8% and 84.6%, respectively, were achieved for the aerobic degradation–ozonation and ozonation–aerobic degradation schemes. However, COD removal during biological pretreatment was as high as 73.6%, thus implying that most of the biodegradable fractions were removed first biologically.

Table 2: Combined Chemical–Biological Treatment of OME (TP: Total Phenols, TC: Total Carbon)

<table>
<thead>
<tr>
<th>Initial conc.</th>
<th>Chemical pretreatment</th>
<th>Biological degradation</th>
<th>Measure of biodegradability</th>
<th>Reference</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD=95 g/l, BOD₅=52 g/l, TP=1.5 g/l</td>
<td>Batch Fenton oxidation at 30 °C and various Fe²⁺ and H₂O₂ concentrations or continuous ozonation at residence times=1.8–8.7 hr and PO₃=0.35–1.21 kPa</td>
<td>Aerated microorganisms in batch reactors at 28 °C</td>
<td>COD and total phenols removal, increase in biomass, Contois rate constants</td>
<td>[25]</td>
<td>+</td>
</tr>
<tr>
<td>COD=34 g/l (OME diluted about three times with distilled water)</td>
<td>Batch ozonation for 8 hr at PO₃=1.73 kPa and 20 °C</td>
<td>Acclimated activated sludge in batch reactors at 28 °C</td>
<td>COD removal, Grau kinetic Constants</td>
<td>[24]</td>
<td>+</td>
</tr>
<tr>
<td>COD=121.8 g/l, TC=34.2 g/l, TP=6.2 g/l</td>
<td>Batch ozonation for 1–7 hr</td>
<td>Anaerobic digestion with mixed acclimated and non-acclimated sludge</td>
<td>Methane and volatile fatty acids production yields</td>
<td>[26]</td>
<td>-</td>
</tr>
<tr>
<td>COD=59.9 g/l, TC = 8 g/l, TP=1.12 g/l</td>
<td>Batch ozonation for 8 hr at PO₃=1.3 kPa and 20 °C</td>
<td>Anaerobic digestion with immobilized acclimated biomass</td>
<td>Methane production yield</td>
<td>[23]</td>
<td>+</td>
</tr>
</tbody>
</table>

From the discussion presented so far, it is evident that OME treatment is a complex issue with no single optimum solution. In view of this, process integration may be a step to the right direction bearing in mind the stringent discharge limits that need to be met.

V. CONCLUSION

Treatment of OME is a complex problem that has not been satisfactorily resolved mainly due to socioeconomic and, to a lesser extent, technological reasons. Several researchers have paid considerable attention in developing environmentally compatible and cost-effective treatment technologies capable of decontaminating what is considered to be a difficult and problematic waste. These technologies commonly comprise aerobic, anaerobic and advanced oxidation processes either alone or in various combinations. A single-stage biological or chemical
treatment is unlikely to achieve complete mineralization at reasonable cost due to the complexity and heavy polluting load of OME. On the other hand, a well-designed sequential treatment consisting of various chemical and biological processes with well-defined treatment objectives may be the optimum solution. The need for such integrated treatments has been recognized recently and research efforts are being directed towards this approach. However, public awareness regarding the fate and environmental implications of OME is perhaps the single most important factor towards the development and operation of full-scale treatment facilities.

REFERENCES


